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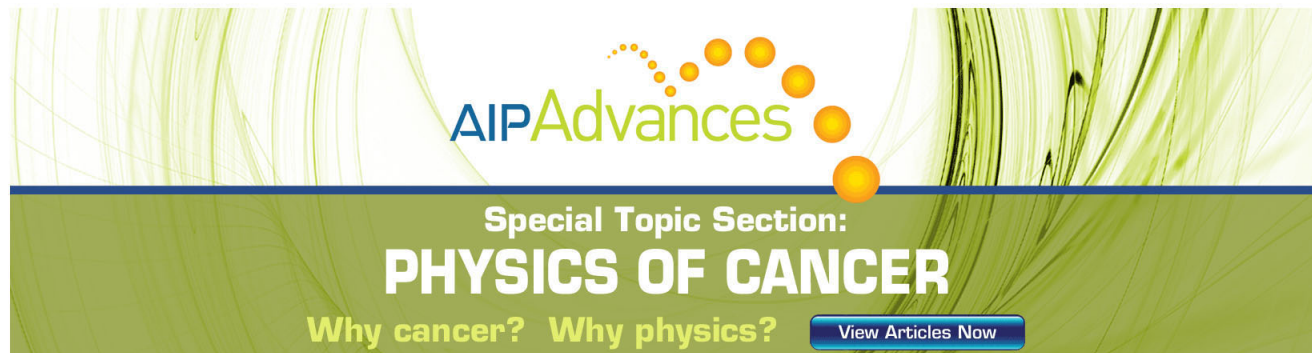
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Phase purity and the thermoelectric properties of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films down to 25 nm thickness

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Thermoelectric phenomena strongly influence the behavior of chalcogenide materials in nanoelectronic devices including phase-change memory cells. This work uses a novel silicon-on-insulator experimental structure to measure the phase and temperature-dependent Seebeck and Thomson coefficients of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films including the first data for films of thickness down to 25 nm. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films annealed at different temperatures contain varying fractions of the amorphous and crystalline phases which strongly influence the thermoelectric properties. The Seebeck coefficient reduces from $371 \mu\text{V/K}$ to $206 \mu\text{V/K}$ as the crystalline fraction increases by a factor of four as quantified using x-ray diffraction. The data are consistent with modeling based on effective medium theory and suggest that careful consideration of phase purity is needed to account for thermoelectric transport in phase change memory. © 2012 American Institute of Physics.
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I. INTRODUCTION

Thermoelectric transport can have a large impact on the performance of semiconductor devices and related nanostructures.^{1–6} The impact is possibly most pronounced in phase-change memories, which experience both large current densities and temperature excursions exceeding 600°C . Recent measurements provided evidence of thermoelectric transport in phase-change cells by capturing a modification in the amorphous region¹ and the programming condition² with the bias polarity. However, there are relatively few data for the thermoelectric properties of phase-change materials at the film thicknesses relevant for contemporary devices.

Past measurements of various chalcogenide materials revealed that holes are responsible for their positive Seebeck coefficient.⁷ The Seebeck coefficient strongly depended on phase and processing conditions. The Seebeck coefficient of rapidly solidified $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was higher than that of water-quenched $\text{Ge}_2\text{Sb}_2\text{Te}_5$ due to grain confinement.⁸ The Seebeck coefficient of bulk $\text{Ge}_2\text{Sb}_2\text{Te}_5$ was measured near 1 mV/K in the amorphous phase⁹ and as low as $20 \mu\text{V/K}$ in the crystalline phase.⁹ Kato and Tanaka¹⁰ measured the Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films in the range 50 nm–600 nm for all three phases from 25°C to 200°C , but only presented the data for 380-nm and 550-nm-thick films, which showed variations of $100 \mu\text{V/K}$ that are large enough to obscure the thickness dependence. Furthermore, the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films can often contain a mixture of amorphous and crystalline phases, and the phase purity can strongly influence transport phenomena.¹¹ However, the existing data for the Seebeck coefficient did not capture the impact of annealing and its impact on phase purity.

The present work measures the Seebeck coefficient of 25-nm and 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films between room temperature and 300°C using an experimental structure in which a buried oxide layer induces lateral temperature fields.^{12,13} This measurement technique contrasts with approaches for capturing the thin-film Seebeck coefficients using a free-

standing membrane and the associated challenging etching steps.^{14–16} Here, we measure the temperature gradient by positioning the temperature sensing metal line at the same distance as the hot junction of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from the heater. This eliminates the heat spreading calibration step required in our previous work¹² and facilitates temperature dependent measurements. The temperature dependence of Seebeck coefficient is explained by different models at each phase, including the effective medium theory (EMT) for treating phase impurities.

II. THERMOELECTRIC PROPERTY MEASUREMENTS

Samples are prepared on an SOI substrate with a $1.5\text{-}\mu\text{m}$ -thick silicon layer and a $1\text{-}\mu\text{m}$ -thick buried oxide layer. A 70 nm-thick silicon dioxide film is deposited on the SOI substrate by plasma-enhanced chemical vapor deposition for electrical passivation. Electrodes are then patterned by e-beam lithography using a 300-nm-thick PMMA resist. A 150-nm-thick platinum film with a 2-nm-thick titanium adhesion layer is deposited by sputtering and lifted off in an acetone bath. Another layer of PMMA resist with e-beam lithography produced patterns for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structures with $0.5 \mu\text{m}$ alignment accuracy. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are deposited by DC magnetron sputtering in argon with a pressure of 2 mT at room temperature and lifted off in an acetone bath. While the as-deposited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is amorphous, crystalline structures in face-centered cubic (fcc) and hexagonal close-packed (hcp) phases are obtained by annealing the samples at elevated temperatures.

In the experimental structure (Fig. 1), the hot junction experiences a large temperature rise while the cold junction is at the substrate temperature. The lateral thermal healing length ($L_h = (k_{\text{Si}}d_{\text{SiO}_2}d_{\text{Si}}/k_{\text{SiO}_2})^{1/2} \sim 13 \mu\text{m}$)¹² is designed longer than the heater-to-junction distance ($1 \mu\text{m}$) and shorter than the length of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film ($60 \mu\text{m}$). This eliminates the need for a second thermometer near the cold junction because the majority of heat dissipates within the thermal healing length. The platinum heater is long enough

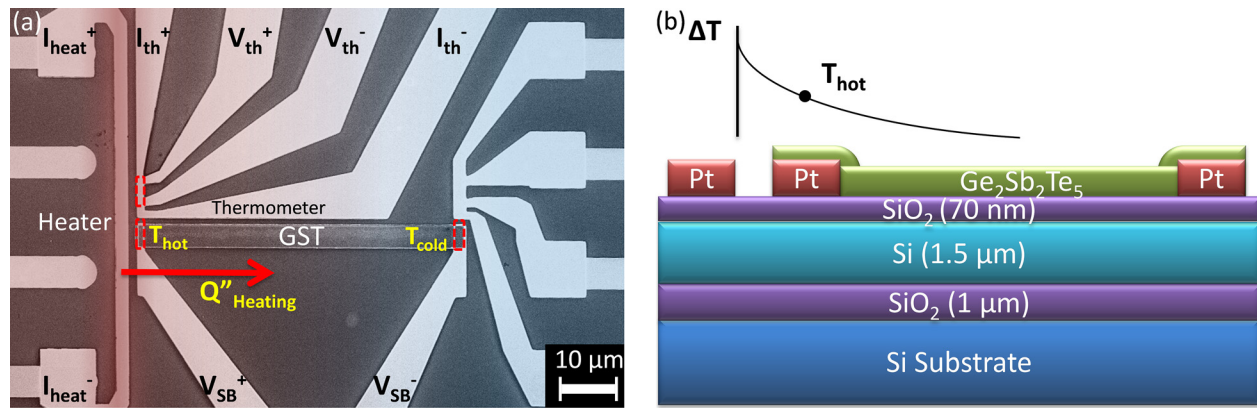


FIG. 1. Top-view SEM image (a) and a cross-sectional schematic (b) of the experimental structure used here for measuring the Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films. The platinum heater, far left, provides uniform heating (Q'') and the temperature gradient necessary for the Seebeck voltage measurements. The optimized thermal healing length of the SOI substrate minimizes temperature rise in the cold junction.

to provide uniform heating across the width of thermometer and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structures. A four-probe-resistance thermometer is located at a symmetric position to the hot junction on the other side of the heater and measures the same temperature as the hot junction. The assumption of symmetry neglects electrode conduction, which is supported by their very large thermal resistance relative to the silicon overlayer. The electrical resistance of thermometer varied linearly from 8.464 Ω to 10.202 Ω at temperature from 25 $^\circ\text{C}$ to 130 $^\circ\text{C}$ with the standard deviation of 0.14 $^\circ\text{C}/\Omega$ to the fitted slope 61.37 $^\circ\text{C}/\Omega$. To increase the temperature sensitivity, the hot junction was heated up to 15 $^\circ\text{C}$ above the substrate temperature. The thermometer was re-calibrated after each annealing process to provide accurate measurements. Measuring the hot junction temperature (ΔT) and the open-circuit voltage (ΔV) across the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structure provides the Seebeck coefficient ($S = \Delta V / \Delta T$). The Seebeck coefficient and the electrical resistivity are successively measured at each temperature controlled by a hot chuck.

The contribution of the platinum electrodes needs to be considered in extracting the Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from the data obtained on the experimental structure. The Seebeck coefficient of bulk platinum has been well characterized in a wide range of temperature.^{27,28} Since the electron mean free path in platinum at room temperature is about 10 nm,^{28,29} we can ignore surface scattering in the 150-nm-thick platinum films. The reported Seebeck coefficient of platinum films reaches constant for thickness above 90 nm.²⁹ Assuming grain boundary scattering is dominant in platinum films, we use the electrical resistivity data to estimate the Seebeck coefficient scaling in platinum films. The Seebeck coefficient of the 150-nm-thick platinum films deviates from the bulk value²⁷ as much as 30%, and this translates into the measurement uncertainties in the Seebeck coefficient up to 4% for the 125-nm and 11% for the 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films.

The as-deposited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are amorphous with no crystal peaks observable in the x-ray diffraction (XRD) measurements (Fig. 2). Because of the large resistance and the associated electrical noise level, we pre-anneal the samples at 130 $^\circ\text{C}$ for 10 min before the measurements. The weak and broad fcc peaks then appear, indicating a partially

crystallized state with phase impurity. The relative change in the (200) peak intensity corresponds to the increase in fcc crystal volume fraction, which can also be predicted by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory. Figure 3 provides the consistent information about the crystal fraction as a function of annealing temperature. Annealing at 190 $^\circ\text{C}$ for 10 min produces fully crystallized fcc $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films with no further change in the peak intensity. The fcc crystals slowly transform into the hcp structure around 300 $^\circ\text{C}$ showing the crystal peaks in both phases. Annealing at 400 $^\circ\text{C}$ for 1 min yields a complete hcp transition.

The electrical resistivity (Fig. 4) and the Seebeck coefficient (Fig. 5) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are measured by following the same pre-annealing and ramping details. Each pre-annealing condition produces a unique fraction of crystals and impurities, verified by the XRD data and the JMAK theory. The phase and temperature dependent Seebeck coefficient data correspond well with the trend in the electrical resistivity data. The effects of pre-annealing indicate that both the properties are strongly dependent on the phase quality.

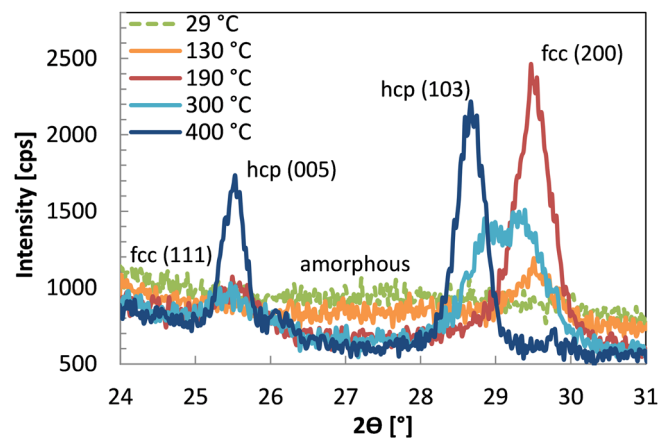


FIG. 2. Impact of annealing on the XRD data for 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films collected using Cu K α radiation. The phase-transition temperature is 130 $^\circ\text{C}$ for the fcc phase and 300 $^\circ\text{C}$ for the hcp phase. Average grain size estimated by the fullwidth at half-maximum increases from 15 nm in the fcc phase to 20 nm in the hcp phase. The 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films show similar phase transitions with higher peak intensities in the crystalline phases.

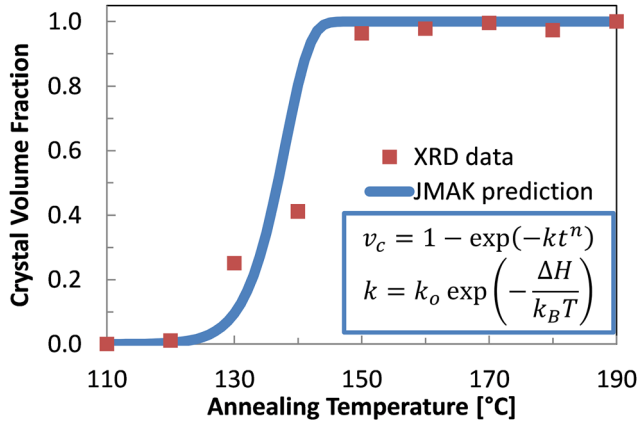


FIG. 3. Crystal volume fraction in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ predicted by the x-ray diffraction peak intensity changes shown in Fig. 2 and the JMAK theory, which accounts for the transformation kinetics as a function of annealing time and temperature. The JMAK crystal fraction (v_c) is extracted using the known annealing time ($t = 10$ min), and the fitting parameters including the Avrami constant ($n = 5$), the crystallization constant ($k_o = 10^{12}$), and the activation energy ($\Delta H = 2.4$ eV).

III. RESULTS AND DISCUSSION

Phase impurities in chalcogenide materials can complicate the prediction of the Seebeck coefficient and require dedicated modeling using, for example, the effective medium theory, as developed later in this section. The classical models, however, with accurate predictions of phase using the XRD measurements can properly capture the temperature dependence of Seebeck coefficient. Our data show that the Seebeck coefficients of amorphous and fcc $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films decrease with increasing temperature. In the case of a homogeneous, non-degenerate semiconductor with single-type carriers, the Seebeck coefficient can be approximated using,^{9,17}

$$S = \frac{k_B}{e} \left(\frac{E_S}{k_B T} + A \right) = \frac{k_B}{e} \left(\ln \left(\frac{N_v}{p} \right) + A \right), \quad (1)$$

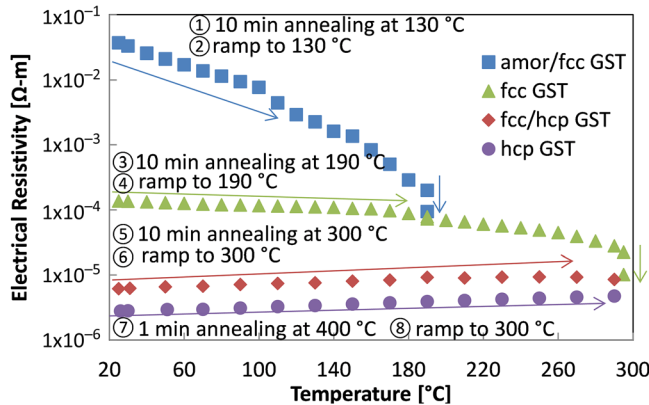


FIG. 4. Temperature and phase dependent electrical resistivity of 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films. After the ramps to 130 °C and 190 °C, additional data are collected at higher temperatures to show crystallization effects. The amorphous and fcc $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films show decreased resistivity with increasing temperature due to enhanced mobility and crystallization process. The resistivity of hcp $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film increases with increasing temperature due to increased scattering with phonons, which is similar to the behavior of metals. The electrical resistivity of 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films (not-shown) is slightly higher but has the same phase and temperature dependence.

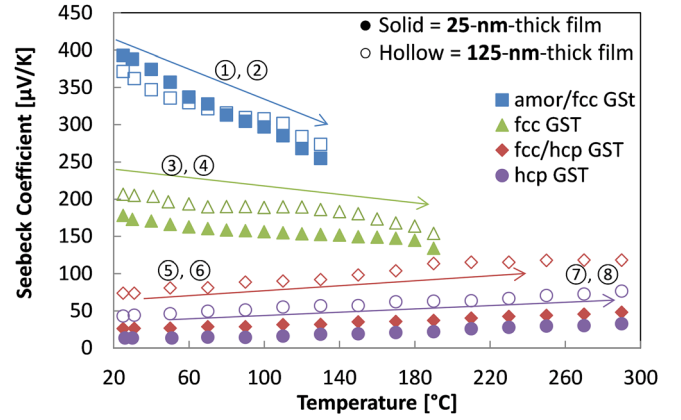


FIG. 5. Temperature and phase dependent Seebeck coefficient of 25-nm and 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films following the same temperature history with the resistivity data (Fig. 3). The partially crystallized $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films, pre-annealed at 130 °C, show no appreciable size effect while the fully crystallized $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films show strong dependence on the film thickness.

where k_B is the Boltzmann constant, A is the transport constant, e is the carrier charge, and E_S is the activation energy, which is related to the carrier density $p = N_v \exp(-E_S/k_B T)$. Increasing temperature activates more carriers, and the increased carrier density results in the decreasing Seebeck coefficient. When the measurement temperature reaches the pre-annealed temperature, the Seebeck coefficient decrease accelerates due to crystallization. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films pre-annealed at 130 °C have $E_S = 0.10$ eV for the 125-nm-thick film and $E_S = 0.16$ eV for the 25 nm-thick film. Their electrical resistivity data with semiconductor relation $\rho = \rho_o \exp(E_\rho/k_B T)$ provide the conductivity activation energies $E_\rho = 0.21$ eV for the 125-nm-thick film and $E_\rho = 0.12$ eV for the 25-nm-thick film. The observed difference in the activation energies ($E_\rho > E_S$) can be attributed to the effect of localized states and mobility activation energy, similar with other reports of chalcogenide materials.¹⁸

The Seebeck coefficient and the electrical resistivity of hcp $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films both increase with increasing temperature, indicating that the material is degenerate semiconductor, as reported previously.^{7,8,10} The Mott formula approximates the Seebeck coefficient in the frame work of nearly free-electrons,^{17,19}

$$S = \frac{\pi^2 k_B^2 T}{3eE_F} (1 + U) = \frac{\pi k_B^2 T}{6e\hbar^2} \left(\frac{8\pi}{3p} \right)^{2/3} (1 + U), \quad (2)$$

where U is a constant that depends on the scattering mechanism, E_F is the difference between the Fermi energy and the band edge. This approximation is valid for spherical Fermi surface that is independent of temperature, as in the free-electron model. A least-square fit to the Seebeck coefficient data after the 400 °C pre-anneal provides $E_F = 0.20$ eV for the 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film and $E_F = 0.32$ eV for the 25 nm-thick film. The deeper Fermi energy levels in the 25 nm-thick film correspond to the carrier density ($p = (2mE_F)^{3/2}/(3\hbar^3/8\pi) \sim 1 \times 10^{20} \text{ cm}^{-3}$) and the hole mobility ($\mu = 1/(\rho ep) \sim 80 \text{ cm}^2/\text{Vs}$) that are larger than those ($p \sim 5 \times 10^{19} \text{ cm}^{-3}$, $\mu \sim 30 \text{ cm}^2/\text{Vs}$) in the 125 nm-thick film. The carrier density difference is consistent with the XRD data where the peak intensity

of the 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film is much higher than that of the 125-nm-thick film. The higher peak intensity indicates a higher concentration of crystals and a larger effective carrier density, which may be responsible for the smaller Seebeck coefficient of the 25-nm-thick films, compared to that of the 125-nm-thick films.

Scattering of carriers on material surface and grain boundaries can strongly influence the transport.^{20,21} However, the carrier mean free path (λ) in crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is much smaller than the film thicknesses or the grain size. A simple estimate for the mean free path using $\lambda = v_{th}\tau$, where τ is the scattering time ($\tau = m^*\mu/q$) and v_{th} is the thermal velocity ($v_{th} = \sqrt{3k_B T/m^*}$), with the experimental hole mobility (μ) and the effective mass (m^*)^{7,10} predicts that the carrier mean free path in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is only a few nanometers. The XRD peak broadening (Fig. 2) estimates that the grain size is about 20 nm in both the 25-nm and the 125-nm-thick films. Neither the grain boundary scattering nor the surface scattering contributes to the thickness dependent Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films.

To observe potential size effect in the electrical resistivity, we have separately prepared 25-nm, 50-nm, 75-nm, and 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films following the same temperature history used for the Seebeck coefficient measurements. The measured electrical resistivities of our $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films above 50 nm are not changing with thickness, consistent with previous finding in films of thickness from 90 nm to 4 μm .²² The Seebeck coefficients of 50-nm-thick or thicker films should therefore exhibit no size effect. On the other hand, the electrical resistivity of 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film is much lower than those of the other films, possibly due to larger carrier density. We attribute this behavior to unusual crystallization phenomena as described in the following paragraph.

A number of studies showed that the crystallization behavior changes as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film thickness scales below 50 nm.^{23–25} The phase-transition temperatures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films with SiO_2 (Ref. 23) or ZnS-SiO_2 (Ref. 24) interfaces decrease with decreasing film thickness. In contrast, the phase-transition temperatures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films with TiN (Ref. 24) or Al_2O_3 (Ref. 25) interfaces increase with decreasing film thickness. The crystallization process is strongly affected by surface energy difference between $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and interfacing materials. Since our $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structures are deposited on SiO_2 surface, we can expect lower phase-transition temperatures with decreasing film thickness. Annealing the 25-nm and the 125-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films at the same temperature can therefore produce higher crystalline quality and larger carrier density in the 25-nm-thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. The thickness dependent carrier density observed in our measurements supports this argument and explains the thickness dependence of Seebeck coefficient.

While the Seebeck coefficient models (Eqs. (1) and (2)) are based on a single-phase assumption, the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films pre-annealed at 130 °C and at 300 °C may contain significant phase impurities. A reasonable way to approximate the Seebeck coefficient of a composite material with different phases is to use the EMT,¹⁷

$$\sum v_i \frac{k_i/S_i - k_{eff}/S_{eff}}{k_i/S_i + 2k_{eff}/S_{eff}} = 0. \quad (3)$$

The parameters v_i , k_i , and S_i are the volume fraction, the thermal conductivity, and the Seebeck coefficient of a phase i , and k_{eff} and S_{eff} are the effective properties. The EMT captures the effective Seebeck coefficient and the effective thermal conductivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film as a function of crystal fraction, which corresponds to the phase purity content (Fig. 6). The thermal conductivity data¹¹ and the Seebeck coefficient data in the pure amorphous phase¹⁰ and the fully crystalline phase provide fitting constraints for matching the data for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film pre-annealed 130 °C to the crystal fraction of ~ 0.25 , which is consistent with the results in Figure 3. The EMT model also predicts that the volume fraction of the hcp phase in the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films pre-annealed at 300 °C is 74% in the 125-nm-thick film and 78% in the 25-nm-thick film. Because the hcp phase is dominant in the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composites, the temperature dependence of Seebeck coefficient follows Eq. (2), rather than Eq. (1). The larger hcp phase volume fraction in the 25-nm-thick film compared to that of the 125-nm-thick film also agrees well with the larger carrier density predictions based on the x-ray diffraction data.

Thermoelectric materials and their properties have drawn attention mostly for its ability to convert heat into electricity. The dimensionless figure of merit ($ZT = S^2 T / k\rho$) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films at room temperature is highest in the fcc phase due to the large Seebeck coefficient and the relatively low electrical resistivity and the thermal conductivity. We estimate the $ZT \sim 0.3$ after the 190 °C pre-anneal using our past thermal conductivity data.^{11,26} Increasing temperature reduces the ZT of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films in the fcc phase but improves the ZT in the hcp phase. Since the Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films in the hcp phase increases linearly with the temperature, the ZT increases by T^3 and up to 0.4 at

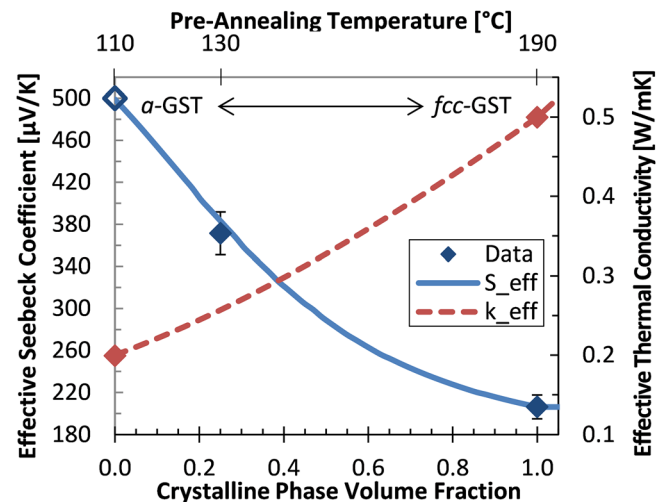


FIG. 6. The Seebeck coefficient and the thermal conductivity of GST films predicted as a function of crystal volume fraction, or the phase purity, using an effective medium model, Eq. (3). Previously reported data^{10,11} for the pure amorphous phase and the fully crystalline phase provide constraints for matching the data for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film pre-annealed 130 °C to the crystal fraction ~ 0.25 . This result is consistent with the XRD analysis in Figure 3.

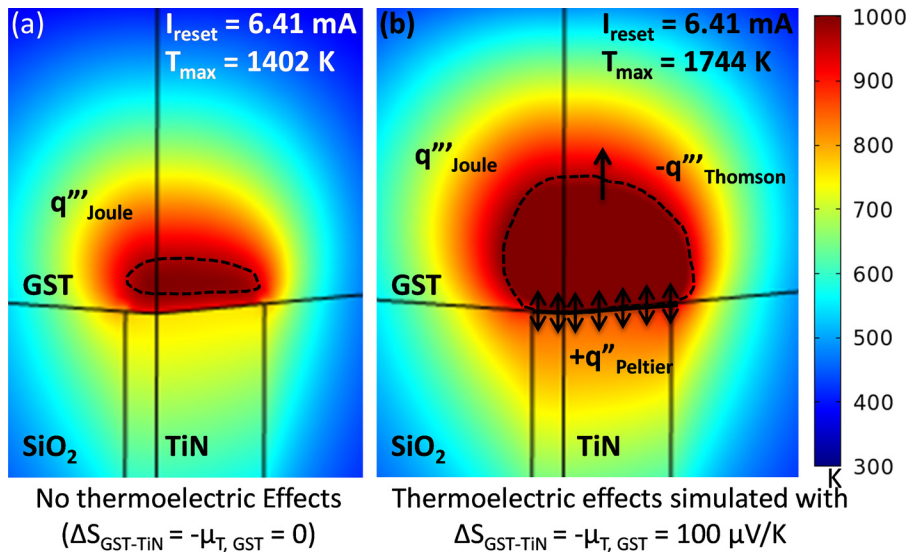


FIG. 7. Predicted impact of thermoelectric transport on the temperature distributions for a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ cell with $50 \text{ nm} \times 200 \text{ nm}$ TiN electrode structure under the programming current 6.41 mA for 50 ns . The thermoelectric effects result in much higher temperature and larger reset resistance, which can significantly lower the writing current. After Lee *et al.*³⁰

300°C . Because the electron contribution to the thermal conductivity is coupled with the electrical conductivity by the Wiedemann-Franz law, the phonon contribution of the thermal conductivity needs to be tuned for further improving the thermoelectric performance.

Thermoelectric properties are particularly important for phase-change memory (PCM) cells because thermoelectric heating can significantly influence the cell temperature distribution (Fig. 7).³⁰ Another thermoelectric property relevant for electronic devices is the Thomson coefficient ($\mu_T = T \partial S / \partial T$), which governs heat absorption or release in a medium carrying an electrical current. The Thomson coefficient of 25-nm -thick $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ranges from -400 to $-500 \mu\text{V/K}$ in the amorphous phase, -50 to $-150 \mu\text{V/K}$ in the fcc phase, and from $+15$ to $+60 \mu\text{V/K}$ in the hcp phase. The Thomson coefficient becomes positive as the material becomes a degenerate semiconductor. The thermoelectric simulations for a mushroom-type PCM cell with a representative Seebeck coefficient $100 \mu\text{V/K}$ and a Thomson coefficient $-100 \mu\text{V/K}$ show that the peak temperature increases up to 44% and the writing current reduces up to 16%. Simulation details are described elsewhere.³⁰

IV. CONCLUSIONS

We report here that the Seebeck coefficient of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films shows strong dependence on temperature and temperature history as governed by the phase purity. The Seebeck coefficient scales with film thickness due to varying degrees of crystallization and phase purity in crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films. The thermoelectric properties identified in this study improve the quality of device simulations that provide a detailed view of temperature distributions. Precise knowledge about thermoelectric transports in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films can thus allow the development of viable design strategies for novel phase-change memories.

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