Thickness and stoichiometry dependence of the thermal conductivity of GeSbTe films

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Thermal conduction in GeSbTe films strongly influences the writing energy and time for phase change memory (PCM) technology. This study measures the thermal conductivity of $Ge_2Sb_2Te_5$ between 25 and 340 °C for layers with thicknesses near 60, 120, and 350 nm. A strong thickness dependence of the thermal conductivity is attributed to a combination of thermal boundary resistance (TBR) and microstructural imperfections. Stoichiometric variations significantly alter the phase transition temperatures but do not strongly impact the thermal conductivity at a given temperature. This work makes progress on extracting the TBR for $Ge_2Sb_2Te_5$ films, which is a critical unknown parameter for PCM simulations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2784169]

Phase change memory (PCM) is emerging as a viable nonvolatile data storage technology.[1] In PCM devices, a phase change material reversibly switches between amorphous and one or more crystalline phases.[2] Phase transitions are thermally activated processes that depend strongly on the temperature evolution during a switching event. During switching devices experience temperatures up to ~650 °C.[3] The increasing emphasis on device scaling and optimization of phase change materials strongly motivates the need for thorough understanding of their thermal properties.[4] This study presents the thickness and temperature dependent thermal conductivity of $Ge_2Sb_2Te_5$ (GST) between 25 and 340 °C in the as-deposited, face-centered-cubic (fcc), and hexagonal close packed (hcp) phases. We also provide conductivity and phase transition data for films with stoichiometry variations ranging from GeTe to $Ge_2Sb_2Te_5$.

This study uses nanosecond laser heating and laser-reflectance thermometry to measure the effective thermal conductivity of metal coated phase change layers between 60 and 400 nm thick deposited on a silicon substrate. A 6 mm diameter, 532 nm wavelength, 6 ns pulse from a Nd:yttrium aluminum garnet laser heats the metal film surface. A 10 mW, 637 nm wavelength, ~10 μm diameter probe beam is focused on the heated portion of the surface.[5] The relative temperature dependent changes in reflectivity yield the normalized surface temperature with submicrosecond temporal resolution.[5–8] Because the heated region is much larger than the probe beam and the sample thickness, we model the thermal response by solving the one dimensional heat diffusion equation in the layered structure assuming a semi-infinite substrate. Fitting the analytical solution of the heat diffusion equation to the measured temperature response extracts the effective thermal conductivity of the phase change layer in the cross-plane direction.[5]

Samples for the temperature and thickness dependent measurement are prepared by rf-sputtering $Ge_2Sb_2Te_5$ films of thicknesses near 60, 120, and 350 nm films on Si wafers using an (AJA International) ATC 1800-F sputtering tool. An ~120 nm Au layer deposited on the phase change film via e-beam evaporation provides the high optical reflectivity at the pump and probe wavelengths required by the thermoreflectance technique. No adhesion layer is deposited between the Au and GST films.

To study the stoichiometry dependence of thermal conductivity and phase transition temperature, six layers of varying stoichiometry are deposited on Si wafers using the ATC 1800-F sputtering tool. GeTe and $Ge_2Sb_2Te_5$ targets are cosputtered to produce the following compositions, measured using x-ray photoemission spectroscopy: GeTe, $Ge_{0.41}Sb_{0.07}Te_{0.52}$, $Ge_{0.31}Sb_{0.14}Te_{0.55}$, $Ge_{0.25}Sb_{0.20}Te_{0.55}$, $Ge_{0.22}Sb_{0.24}Te_{0.54}$, and $Ge_2Sb_2Te_5$. An ~80 nm aluminum film deposited via rf sputtering in the same system enables the thermoreflectance measurement.

Figure 1 shows cross section images of the ~60 nm as-deposited and hcp films taken via scanning electron microscopy. X-ray diffraction measurements confirm the phase transition from as deposited to fcc at ~130 °C and the transition from fcc to hcp at ~200 °C, consistent with the results of Yamada *et al.*[9] The hcp phase shown in Fig. 1 was obtained by annealing the as-deposited sample at 340 °C for 20 min. The images show a thickness decrease from 65 to 60 nm in the transition from the as deposited to hcp phases. We attribute the reduction in thickness to the increase in density of the crystallized material. Wiedenhof *et al.*[10] reported similar density increases of 6.2% ±.8% in the transition from as deposited to crystalline phases of $Ge_2Sb_2Te_5$.

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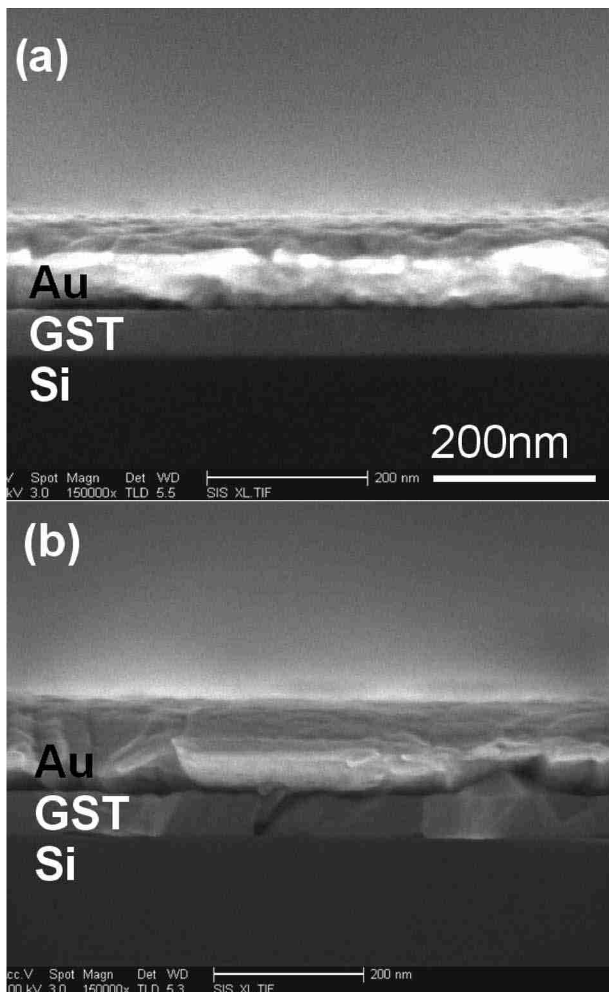

FIG. 1. Cross-section images of a sample in the (a) as-deposited and (b) hexagonal close packed phases taken by scanning electron microscope.

Kim *et al.*[11] and Giraud *et al.*[12] reported similar fractional changes in thickness upon crystallization.

Figure 2 shows the effective thermal conductivity as a function of temperature, phase, and GST layer thickness. For the 350 nm thick sample, at room temperature, we measure thermal conductivities of 0.29, 0.42, and 1.76 W/m K in the as-deposited, fcc, and hcp phases, respectively. The room temperature thermal conductivities for the ~60 nm film are 0.17, 0.28, and 0.83 W/m K in the respective phases. These values are similar to the previously reported values which vary from 0.17 to 0.34,[3,13] 0.26 to 0.95,[12,14] and 1.40 to 1.57 W/m K (Ref. 14) in the respective phases.

The average relative errors across all thicknesses are 7.2%, 8.7%, and 9.3% for the as-deposited, fcc, and hcp phases, respectively. We attribute the increases in error with increasing thermal conductivity to the increased relative significance of the measurement noise associated.

The thickness variation of the thermal conductivity can be due to boundary resistances and variations in microstructural quality. This can be investigated using a simple model that separates a minimum internal resistance R_{int} from the boundary resistance R_B and the extra internal resistance due to microstructural defects R_{defects}:

$$R_{\text{net}} = R_{\text{int}} + R_{\text{defects}} + R_B. \tag{1}$$

Assuming that the internal thermal conductivity k_{int} is independent of the layer thickness, Eq. (1) may be rewritten as

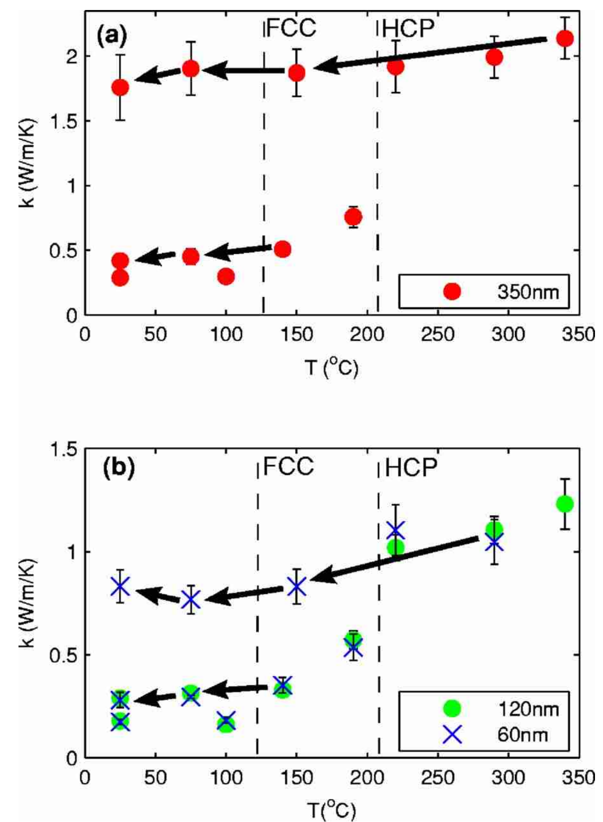

FIG. 2. (Color online) Effective thermal conductivity of $Ge_2Sb_2Te_5$ vs temperature for (a) ~350 nm and (b) ~60 and 120 nm films. The dashed lines indicate the phase transition temperatures. The arrows show the temperature hysteresis due to phase change, measured by ramping the temperature back to room temperature after heating to 150 and, subsequently, to 340 °C.

$$\frac{d}{k_{\text{eff}}} = \frac{d}{k_{\text{int}}} + R_{\text{defects}} + R_B, \tag{2}$$

where d is the layer thickness and k_{eff} is the measured effective thermal conductivity. The assumption that k_{int} is independent of thickness is justified when the layer thickness is much greater than the heat carrier mean free path, which is satisfied here.[11,14]

In this model, the local slope of $1/k_{\text{eff}}$ vs $1/d$ indicates the combined magnitude of boundary and defect resistances R_B and R_{defects}. When analyzed assuming a thickness independent boundary resistance, the data show a nonlinear dependence on $1/d$, indicating that the microstructural contributions to the thermal resistance are thickness dependent. Characteristic magnitudes of this slope for the as-deposited and hcp phases are $\sim 10^{-7}$ and $\sim 10^{-8}$ m^2 K/W, respectively, with values in the fcc phase lying between these limits. The slope for the as-deposited phase is significantly larger than the previously measured values for thermal resistances, while the slope for the hcp phase is of similar magnitude to measured values.[11,15] These observations suggest that interface resistance alone cannot account for the thickness dependence of the effective thermal conductivity.[16] The decreased magnitude of the slope after crystallization and annealing may be caused by reduction in the quantity of interface defects[17] and enhanced physical contact and adhesion due to annealing.[11]

Figure 3 shows the effective thermal conductivity of layers of six stoichiometric compounds produced by cosputtering GeTe and $Ge_2Sb_2Te_5$. The effective thermal conductivity of all compounds in the as-deposited phase is between 0.16

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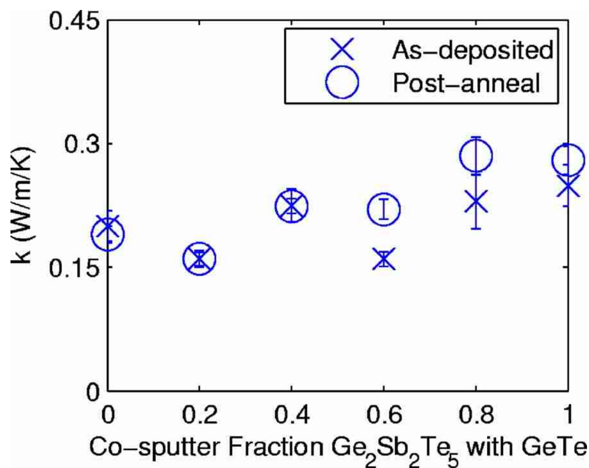

FIG. 3. (Color online) Effective thermal conductivity at 75 °C of six stoichiometric compounds in the as-deposited phase and after annealing at 150 °C for 15 min. Compounds are produced by cosputtering $Ge_2Sb_2Te_5$ with GeTe. $Ge_2Sb_2Te_5$ and the two compounds closest in stoichiometry crystallized during annealing, leading to larger values of thermal conductivity. Scanning electron microscopy images show thicknesses of the as-deposited samples vary between 235 and 413 nm.

and 0.25 W/m K with relative errors between ±5.0% and ±14.3%. X-ray diffraction measurements of $Ge_2Sb_2Te_5$ and the two compounds of closest stoichiometry confirm these samples crystallized after a 15 min 150 °C annealing. Compared to the as-deposited phase, the crystalline compounds exhibit larger thermal conductivities of 0.22, 0.29, and 0.28 W/m K for $Ge_{.25}Sb_{.20}Te_{.55}$, $Ge_{.22}Sb_{.24}Te_{.54}$, and $Ge_2Sb_2Te_5$, respectively.

Table I shows the crystallization temperature and as-deposited thickness for each of the six compounds. The phase transition temperature from as deposited to crystalline increases monotonically as the fraction of Sb decreases in the compound. This is consistent with calculations by Lankhorst,[18] which predict that transition temperatures increase with increasing bond enthalpies and coordination numbers. This suggests that the decrease in transition temperature is due in part to the threefold coordination of Sb relative to the fourfold coordination of Ge in the amorphous material.[19,20]

TABLE I. Measured compositions, targeted cosputter fraction of $Ge_2Sb_2Te_5$, thicknesses, and phase transition temperatures for the six stoichiometric compounds.

Composition	Targeted $Ge_2Sb_2Te_5$ cosputter fraction (%)	As-deposited thickness (nm)	First as deposited to crystalline transition temperature (°C)
GeTe	0	327	180
$Ge_{0.41}Sb_{0.07}Te_{0.52}$	20	235	171
$Ge_{0.31}Sb_{0.14}Te_{0.55}$	40	400	158
$Ge_{0.25}Sb_{0.20}Te_{0.55}$	60	268	146
$Ge_{0.22}Sb_{0.24}Te_{0.54}$	80	345	131
$Ge_2Sb_2Te_5$	100	413	127

In summary, these results illustrate the temperature, phase, and thickness dependence of the effective thermal conductivity of $Ge_2Sb_2Te_5$ layers. The data show that a fixed thermal interface resistance alone cannot explain the trends in thickness dependence, though it may be the most significant factor in the thickness dependence of annealed and crystallized films. Additionally, the thermal conductivity of the as-deposited phase does not depend strongly on stoichiometry for compounds varying between GeTe and $Ge_2Sb_2Te_5$. The phase transition temperatures, however, may be tailored by changing the fraction of Sb in the phase change material.

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