

Thermal Conductivity Measurements of Sb–Te Alloy Thin Films Using a Nanosecond Thermoreflectance Measurement System

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Using a nanosecond thermoreflectance measurement system, which enables the measurement of the thermal conductivity of nanometer-scale thin films, we have measured the thermal conductivities of Sb₂Te, Sb₂Te₃, SbTe₉, Sb, and Te thin films at room temperature. We clarified that the thermal conductivities of Sb–Te alloys depend on the Sb and Te atomic ratios. A large change in thermal conductivity was observed in the vicinity of the composition ratio of Sb₂Te₃. We proposed that this large change may be attributable to the formation of an Sb atomic network in the crystalline structure of the Sb–Te alloy.

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The thermal properties of optical and electrical phase-change memory constituents are very important for the development of new as well as the optimization of current memory designs. In optical memory, the readout,^{1–6} recording, and erasure⁷ processes are strongly related to laser heating. In electrical phase-change memory, Joule heating or indirect heating induces an amorphous–crystalline transition in the phase-change material used.⁸ The thermal properties of the materials making up a memory device are therefore critical factors in device operation and must be investigated for effective device design. Moreover, the measurement of the absolute values of these thermal parameters is essential in order to obtain reliable results from numerical simulations of temperatures inside active devices.

We have reported previously on the temperature dependences of the thermal and optical properties of optical disk materials, namely, chalcogen and dielectric materials.^{9–12} In this paper, we report on the thermal conductivities of three different Sb–Te alloy thin films (in the low-temperature crystalline state) as well as those of Sb and Te at room temperature. Sb–Te alloys are widely used as recording media for optical disks, as the functional layer of super-resolution disks,^{13,14} and as resistive-element materials in phase-change memory.⁸ The thermal conductivity was measured using a nanosecond thermoreflectance measurement system (Nano-TheMS), a novel apparatus that can measure the thermal conductivity of nanometer-order thin films.^{15,16}

Sb₂Te, Sb₂Te₃, and SbTe₉ were selected as representative Sb–Te alloys and their corresponding thermal conductivities were measured and compared with those of pure Sb and Te. All materials investigated were fabricated by RF magnetron sputtering and had 200 nm of TiN deposited on both sides of the material being measured; glass substrates were used. The sample structure is shown in Fig. 1. The samples were grown using the following sputtering conditions: the base pressure, inlet gas, and sputtering pressures were 5×10^{-4} Pa, argon, and 0.5 Pa, respectively. The RF powers used were 200 W for TiN and 100 W for the deposition of Sb–Te alloys. TiN served as an effective diffusion barrier and its thermoreflectance signal intensity was sufficient to deter-

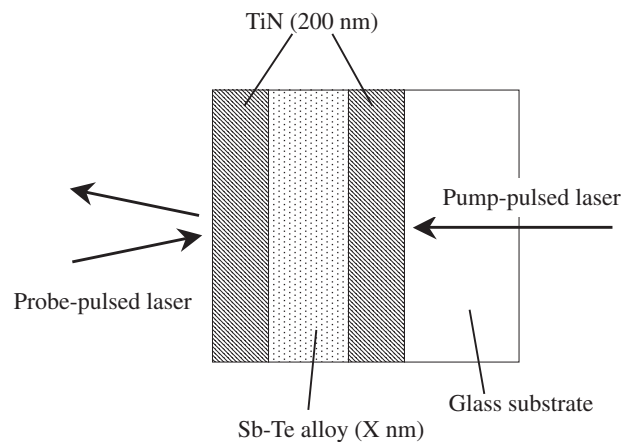


Fig. 1. Cross-sectional view of the sample and configuration of incident pulsed lasers. The thickness X nm is 400 nm for Sb₂Te₃, SbTe₉, and Te, and 1 μ m for Sb and Sb₂Te.

mine the transmitted heat flux in the Nano-TheMS.¹⁰ The thicknesses of the Sb–Te alloys were 400 nm for Sb₂Te₃, SbTe₉, and Te, and 1 μ m for Sb and Sb₂Te. Slightly thicker films of Sb and Sb₂Te were used for performance reasons of the Nano-TheMS because the thermal conductivities of these two materials are approximately $10 \text{ W m}^{-1} \text{ K}^{-1}$ or higher, and the time resolution of the Nano-TheMS is not sufficient to ensure their thermal conductivities at 200–300 nm thickness. All samples except for the Te sample were annealed at 300 °C for crystallization and to relax the interfacial stress. Because the 300 °C annealing of the Te sample resulted in sample damage, the Te sample was annealed at 200 °C. All annealing processes were carried out in Ar gas ambient to avoid oxidization.

The principle of the Nano-TheMS is as follows. A pump-pulsed laser is incident from the glass side of the substrate and heats up the nearest TiN film layer (see Fig. 1). The heat generated then propagates to the opposite side and the transmitted heat affects the reflectivity of the TiN layer on the opposite side. The change in reflectivity as a function of time is detected using a second probe laser. The reflectivity change strongly depends on the thickness of the sample, and the thermal conductivity can be determined by analyzing the rise time of the probe laser. Detailed descriptions of the

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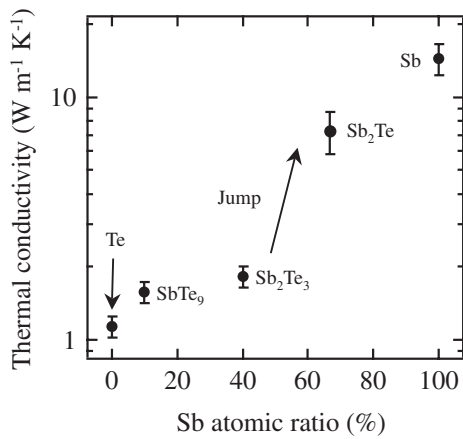


Fig. 2. Thermal conductivities at room temperature for each Sb–Te alloy.

principles of the Nano-TheMS,^{15–19} experimental setup, and related conditions regarding this measurement technique have been previously published.^{9–11} All experiments were carried out at room temperature and in Ar gas ambient to avoid oxidization. For analysis of the thermal conductivity, the specific heat capacity and the density of all materials should also be required. These parameters were determined by differential scanning calorimetry and X-ray reflectometry, respectively.

Figure 2 shows the thermal conductivities of the Sb–Te alloys as well as those of pure Sb and Te. The vertical and horizontal axes show the thermal conductivity on a logarithmic scale and Sb/Te atomic composition ratio, respectively. With increasing Sb/Te ratio, the thermal conductivity gradually increased to approximately $2 \text{ W m}^{-1} \text{ K}^{-1}$ in the case of Sb_2Te_3 ; however, the thermal conductivity of Sb_2Te suddenly increased to approximately $8 \text{ W m}^{-1} \text{ K}^{-1}$. From Fig. 2, it can be seen that SbTe_9 and Sb_2Te_3 show a thermal conductivity characteristic similar to that of Te, while the thermal conductivity of Sb_2Te is more similar to that of Sb. Kifune *et al.* studied the crystal structure of Sb–Te alloys from pure Sb to Sb_2Te_3 by increasing the Te atomic ratio.²⁰ They found that an Sb-like layer exists in the crystal structure for Sb/Te ratios larger than Sb_2Te_3 ; but for Sb_2Te_3 , no Sb layer is present. This implies that the physical properties of Sb_2Te_3 tend to be Te-like. Their results are consistent with the observed sudden increase in the thermal conductivity from Sb_2Te_3 to that of Sb_2Te .

The thermal conductivities of the pure Sb and Te films were 14.0 and $1.1 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. These values are approximately half those of bulk Sb and Te, whose thermal conductivities are approximately 23 and $4 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, respectively.²¹ Taketoshi *et al.* already reported that the thermal diffusivities of aluminum and molybdenum thin films are lower than their bulk values. They attributed the decrease to macroscopic structural

differences between the thin film and the bulk. We measured the densities of the Sb and Te films by X-ray reflectometry to compare them with those of bulk Sb and Te, which were 6.69 and 6.25 g cm^{-3} , respectively.²² Results showed that the densities of the Sb and Te films were 6.3 and 5.9 g cm^{-3} , respectively, which are lower than their bulk values. The lower densities may lead to the lower measured thermal conductivities.

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