Room-temperature fast deposition and characterization of nanocrystalline Bi$_{0.4}$Sb$_{1.6}$Te$_3$ thick films by aerosol deposition

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Abstract. P-type nanocrystalline Bi$_{0.4}$Sb$_{1.6}$Te$_3$ thick films were directly deposited on copper substrates by aerosol deposition (AD) involving shock compaction of the starting powder at room temperature. The film deposition rate was over 700 µm/min. The relative density of the films was above 95%. Films with a thickness of over 2 mm were obtained. They consisted of nanocrystals with grain sizes of several tens of nanometers. The crystal structure of the films was the same as the bulk materials prepared by spark plasma sintering (SPS) using the same starting powder. We measured the electrical conductivity, carrier concentration, Hall mobility, and thermal conductivity of the films and compared them with those of the bulk materials. The thermal conductivity of the AD film was 20–30% lower than that of the bulk materials, which is attributed to the increased number of grain boundaries and some defects in the AD films.

1. Introduction
Thick film thermoelectric devices used for localized and decentralized energy harvesting are important for making compact or large-area thermoelectric generators (TEGs) that operate at very small temperature differences. TEGs have attracted extensive interest for several decades because of the following unique features: no moving parts, quiet operation, low environmental impact, and high reliability [1]. The performance of a thermoelectric material is evaluated by its dimensionless thermoelectric figure of merit ($ZT$). Here, $Z = S^2\sigma/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical resistivity, $\kappa$ is the thermal conductivity, and $T$ is the absolute temperature. Furthermore, $\kappa$ is the sum of two independent components: an electronic contribution $\kappa_e$ and a phonon contribution $\kappa_p$ ($\kappa = \kappa_e + \kappa_p$). To estimate the $\kappa_p$ value, the $\kappa_e$ value is often obtained by assuming the validity of the Wiedemann–Franz law $\kappa_e = LT\sigma$, where $L$ is the Lorenz number. Almost all thermoelectric materials are small band gap semiconductors with carrier concentrations of the order of $10^{19}$–$10^{21}$ cm$^{-3}$ (depending on the material system); these carrier concentrations are intermediate between those of metals and insulators. For this reason, it has been suggested that the ideal thermoelectric material is amorphous to phonons while maintaining high electron mobility, the so-called ‘phonon glass electron crystal’ [1]. Until now, bismuth telluride (Bi$_2$Te$_3$) and its alloys with antimony telluride (Sb$_2$Te$_3$) and bismuth selenide (Bi$_2$Se$_3$) have been considered the best...
thermoelectric materials near room temperature. They can generate power from low-quality energy sources such as low-temperature waste heat. The $ZT$ value of these materials is around unity at low temperatures (i.e., between room temperature and about 100°C); no other practical materials that have a $ZT$ value significantly above unity have been discovered for almost 50 years [2]. Recently, p-type nanocrystalline bismuth antimony telluride (Bi$_x$Sb$_{2-x}$Te$_3$, $x = 0.4$ and 0.5) bulk materials fabricated by hot pressing of ball-milled nanopowders with an average size of about 20 nm were found to have a peak $ZT$ of 1.4 at 100°C and about 1.2 at room temperature [3]. This high $ZT$ is reported due to a low lattice thermal conductivity caused by increased phonon scattering from grain boundaries and defects. While thermoelectric research has focused on the synthesis of novel and efficient bulk materials [4], film manufacture has received less attention.

We have recently been investigating various films of electronic materials such as ceramics, metals, and composites formed by aerosol deposition (AD) [5]. In AD, a powder is mixed with a carrier gas such as nitrogen or air to form an aerosol jet, which is ejected through a nozzle installed in a deposition chamber via a narrow slit onto substrates. AD is based on shock compaction of particles in starting powders at room temperature, known as room-temperature impact consolidation (RTIC). In RTIC, the aerosol jet enables deposition of high-density ceramic, metal, and composite films that are less than 1 µm thick to several hundreds of micrometers thick on various substrates such as glass, metal, ceramic, and plastic in a few minutes at room temperature. We previously found that aerosol-deposited films (AD films) are likely to have low thermal conductivities because they have nanocrystalline grains and defects that increase the phonon scattering [6]. In this study, we deposited Bi$_{0.4}$Sb$_{1.6}$Te$_3$ films onto copper (Cu) substrates by AD and investigated their thermoelectric properties (i.e., electrical conductivity, carrier concentration, Hall mobility, and thermal conductivity).

2. Experimental procedure

2.1. Sample preparation

P-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ films were directly deposited on 1-mm-thick Cu substrates by AD at room temperature. Bi$_{0.4}$Sb$_{1.6}$Te$_3$ with a purity of over 99.9%, which was obtained from commercial suppliers in powder form (200 mesh or smaller), was used as the starting powder. Figure 1 shows a schematic diagram of the experimental setup. The starting powder was mixed with a carrier gas (nitrogen, N$_2$) and then an aerosol was formed an aerosol chamber. The aerosol was transported through a tube to a slit nozzle with an orifice size of 20 mm × 0.5 mm installed in a deposition chamber, which was evacuated by a mechanical booster pump and a rotary pump in series. The aerosol jet was ejected from

![Figure 1. Schematic diagram of the aerosol deposition equipment.](image-url)
the slit nozzle due to the pressure differential between the aerosol and the deposition chambers. The Cu substrate, which was located at 10 mm from the nozzle exit, was set on the substrate holder and was then horizontally reciprocated at a scanning speed of 0.1 mm/s. The deposition chamber pressure was approximately 1 kPa during deposition. After deposition, the film surface was mechanically polished using 800–2000 grade emery paper. Figure 2 shows a photograph of an example of a Cu substrate and an as-deposited film. For comparison, bulk materials were sintered from the same starting powder by spark plasma sintering (SPS) at 450°C for 5 min at a pressure of 40 MPa in an argon atmosphere.

2.2 Sample characterization
The film deposition rate was determined by thickness measurements using a surface texture measuring instrument. The sample density was measured using the Archimedes method. The crystallinity of the samples was analyzed by X-ray diffraction (XRD) with Cu Kα radiation in the 2θ range of 10–80°. The electrical conductivity (σ) of the samples was obtained by the direct-current four-probe method. The thermal diffusivity of the samples was measured by the laser flash method. The heat capacity of the samples was measured using a differential scanning calorimeter. The thermal conductivity (κ) of the samples was calculated from the thermal diffusivity (α), the heat capacity (C_p), and the density (ρ) using the equation κ = αC_pρ. All measurements were performed at temperatures between room temperature and 300°C. The carrier concentration (n) of the samples was measured by the van der Pauw method at a magnetic field strength of 9 T between room temperature and 127°C. The carrier mobility of the samples was calculated by the equation μ = (ne/σ)^-1, where e is the electron charge. The microstructures of the samples were examined by transmission electron microscopy (TEM) at an operating voltage of 200 kV.

3. Results and discussion
As shown in Figure 2, Bi_{0.4}Sb_{1.6}Te_{3} films that had been directly deposited on Cu substrates had a thickness of above 2 mm; the film deposition rate was approximately 700 µm/min. Figure 3 shows a photograph of an example of the appearance of polished film and the bulk material. The surface of the polished film had a metallic luster. This is thought to be because the AD films, which have dense crystal structures consisting of crystal grains of the order of several tens of nanometers, have a surface roughness of a few nanometers without grain dropout by surface polishing. The relative density of the film was 97.6% of the theoretical density. In contrast, the bulk material had a relative density of 90.1%.
Figure 4 shows typical XRD patterns of the AD film and the bulk material. The patterns of the starting powder are also shown. Comparison with the powder diffraction file (#72-1836) shows that the XRD patterns of both the AD film and the bulk material can be attributed to the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ phase. The lattice parameter values of the AD film and the bulk material are 3.23 and 3.22 Å, respectively, which are very similar. The crystallite size ($D$) was evaluated using the Scherrer formula $D = 0.94\lambda/(\beta \cos \theta)$, where $\lambda$ is the X-ray wavelength, $\beta$ is the angle in radians at which the intensity is half the maximum intensity (FWHM), and $\theta$ is the angle at which the intensity is maximum. The crystallite sizes evaluated using the Scherrer formula for the AD film and the bulk material are 26.8 and 30.0 nm, respectively; hence, the AD film had a smaller crystallite size than the bulk material. This result indicates that the fracture and consolidation of the starting powder resulted in the reduction of the crystallite size in the AD films. These results are consistent with the metallic luster surface of the AD film (see Figure 3).

Figure 5 shows the temperature dependencies of the electrical conductivity of the AD film and the bulk material. The electrical conductivity of the AD film gradually increases with increasing temperature, showing typical semiconductor behaviour, while that of the bulk material decreases with increasing temperature. The electrical conductivity of the AD film was at least one order of magnitude less than that of the bulk material. As is well known, electrical conductivity depends on the carrier concentration and mobility according to $\sigma = ne\mu$. Figure 6 shows the temperature dependence of the carrier concentration and Hall mobility of the AD film and the bulk material. This data reveals that both the AD film and the bulk material are p-type. The carrier concentration of the AD film was comparable to that of the bulk material. This is probably because defects (e.g., point defects and dislocations) increase the carrier concentration. Therefore, the reduction in the electrical conductivity shown in Figure 5 is due to a reduction in the Hall mobility. In both the AD film and the bulk material, the carrier concentration and the Hall mobility are almost temperature independent. Further study is needed to determine more precise temperature dependencies of the carrier concentration and the Hall mobility of the AD film and the bulk material by considering electrode formation for Hall measurements.

Figure 7 shows the temperature dependencies of the total and lattice thermal conductivities for the AD film and the bulk material. The total thermal conductivity ($\kappa$) can be written as $\kappa = \kappa_e + \kappa_p$, where $\kappa_e$ and $\kappa_p$ are the electronic and lattice thermal conductivities, respectively.
where \( \kappa_e \) and \( \kappa_p \) are electron and phonon components. The former can be roughly calculated from experimental values of the electrical conductivity using the Wiedemann–Franz law (\( \kappa_e = L T \sigma \)), where \( L \) is the Lorenz number (\( 2.44 \times 10^{-8} \text{ V}^2\text{K}^{-2} \)) and \( T \) is the absolute temperature. Both the total and lattice thermal conductivities initially decrease and then increase with increasing temperature. At low temperatures, phonon–phonon scattering is enhanced due to the reduction in the lattice thermal conductivity with increasing temperature as a result of enhanced lattice vibrations. However, with a further increase in temperature, bipolar diffusion of electrons and holes arising from intrinsic radiation will result in an additional thermal conductivity, thereby increasing the lattice thermal conductivity [7]. In the AD film, the lattice thermal conductivity accounted for 89–95% of the total thermal conductivity because of the reduction in the electrical conductivity (see Figure 5).

Figure 8 shows TEM images of the AD film and the bulk material. The AD film had a grain size ranging from a few to several tens of nanometers. In contrast, the grain size of the bulk material was several hundreds of nanometers due to grain growth by Ostwald ripening. The grain size differs from the crystallite size, which was obtained from XRD patterns (see Figure 4), since a single grain can be...
composed of several crystallites. Therefore, the reduction in the electrical conductivity and the thermal conductivity in the AD film may be attributed mainly to increased carrier and phonon scattering, respectively, by the many grain boundaries induced by nanocrystals. We are currently measuring the recovery of the electrical conductivity of the AD film on post-annealing of the film. It has been reported that to minimize carrier scattering by the grain boundaries, nanometer-sized grains with the same phase as bulk materials should be used to reduce the band edge offset [8, 9]. The carrier transport processes in AD films need to be better understood to prevent nanocrystals from increasing the electrical conductivity.

To check the feasibility of the AD films for use in thermoelectric generator modules, we measured their Seebeck coefficient (the thermoelectric power of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across a material). The Seebeck coefficients of the AD film and the bulk material at a temperature of 100°C were about 150 and 200 µV/K, respectively. By assuming a charge-carrier scattering distance of energy, the Seebeck coefficient at a low temperature can be expressed as:

$$S = \frac{8\pi^2 k_B^2}{3e h^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3},$$

where $k_B$ is the Boltzmann constant, $h$ is the Plank constant, $m^*$ is the effective mass, and $n$ is the carrier concentration. Thus, the Seebeck coefficient decreases with increasing carrier concentration [7]. In general, Bi$_{0.4}$Sb$_{1.6}$Te$_3$ materials prepared at room temperature (such as the AD films) have many point defects; hence, a post thermal treatment required to eliminate them [10]. The Seebeck coefficient of the films may be enhanced due to the reduction in the carrier concentration due to there being fewer defects, which act as acceptors [11]. Holes in the AD films are scattered by the grain boundaries and defects; hence, they may be prevent the realization of an improved $ZT$. To further improve the thermoelectric films produced by AD, it is necessary to control the number of nanocrystals-grains and suppress defects to reduce the thermal conductivity and increase the electrical conductivity and the Seebeck coefficient.

4. Conclusions

To develop a thick-film TEG, we have prepared Bi$_{0.4}$Sb$_{1.6}$Te$_3$ films deposited on Cu substrates by AD. The AD films were directly deposited on the substrates at room temperature. They had a thickness of
over 2 mm. The deposition rate of over 700 µm/min was obtained. The surface of the polished films, which has a relative density of 97.6%, has a metallic luster. XRD and TEM analyses revealed that the obtained films have dense crystal structures consisting of grains with sizes ranging from a few to several tens of nanometers. Consequently, the thermal conductivity of the film is 20–30% lower than that of the bulk materials. The AD films increase the thermoelectric figure of merit (ZT) by about 70–80%. The electrical conductivity of the films was at least one order of magnitude lower than that of the bulk material. These results suggest that grain boundaries and defects in the AD film affect both phonon conduction and electron conduction. We intend to confirm the recovery of electrical conductivity by heat treating the films.

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