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Bi_2Te_3 Thin Films Grown by Magnetron Sputtering

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Abstract. Bi_2Te_3 thin films grown the substrate with 80 nm in diameter have been prepared by using magnetron sputtering technique. The structure of thin films was determined by X-ray diffraction experiments. The average grain size and particle size in these powers were measured by the line profile analysis method of X-ray diffraction patterns and by scan electron microscopy, respectively. The thin films were investigated by using SEM measurements. The results indicate that Bi_2Te_3 alloys could be potentially important TE materials for many applications, especially for prolonged TE device operation at high temperatures, such as for recovery of waste heat from automobile, aircrafts, and power plants due to their superiorphysical properties, including the ability of operating at high temperature/high power conditions, high mechanical strength and stability, and radiation hardness.

Introduction

Approximately, 90% of the world's power is generated by heat engines that use fossil fuel combustion as a heat source and typically operate at 30%–40% efficiency. A significant proportion of heat is lost to the environment. Co-generation plants have been used to improve the overall efficiency by providing electricity as well as heat for heating purposes. This heat or heated fluids are transported in pipes for many industrial and residential applications. Wireless sensors such as steam/gas-leak sensors, pressure sensors, and temperature sensors are often used for condition monitoring of such pipes. The power requirements for these sensors are few microwatts and primary batteries are used to meet this demand. However, batteries have limited lifetime. Battery replacement cost and labor cost make large scale use of these sensors infeasible. Thermoelectric modules, which utilize the temperature difference between the hot pipe and the ambient air to generate power, can be used for powering these sensors. Existing pick and place and micro fabrication techniqueshave limited cost-effective scalability for manufacturing of application-specific TEGs. These solid state thermoelectric generators (TEGs) are reliable, silent, environmental friendly, and could play an important role in a global sustainable energy solution. TEGs utilizing waste heat to generate power should be low-cost in order to be competitive with other technologies [1].

In thermoelectric generators, the seebeck effect is used for the direct conversion of a temperature difference into an electric potential between a material pair junction and the thermocouple. The performance of TE materials is characterized by the TE figure of merit *ZT*. While there is no fundamental upper limit to *ZT*, progress has been extremely hard to come by, mainly due to the coupling between *S*, and K-changing one parameter would alter the others. There has been much attention drawn to finding TE materials suitable for solid-state refrigeration and power conversion. In particular, thin film TE materials are of great interest because they offer the potential for direct integration of microcoolers power generators with various photonic and electronic devices.

Bi_2Te_3 bulk materials are the best choice for thermoelectric applications at room temperature due to their large thermoelectric figure of merit $ZT = (S^2r/k)T$ of about 1 at T = 300 K. In bulk materials, an increase of ZT beyond 1 is difficult to achieve since the transport properties depend on each other, being given by fundamental parameters of the electron and phonon system. Hicks and Dresselhaus predicted a ZT enhancement in lowdimensional system due to quantum confinement and lattice phonon scattering[1]. Venkatasubramanian et al. reported hole-conducting Bi_2Te_3 and electron-conducting $Bi_2Te_3/Bi_2(Te0.94Se0.06)3$ superlattice structures epitaxially grown on GaAs substrates by metalorganic chemical vapor deposition (MOCVD), yielding ZT of 2.4 and 1.7, respectively[2]. Electron-conducting Bi_2Te_3 thin films and Bi_2Te_3/Bi_2(Te0.88Se0.12)3 superlattices were epitaxially grown on BaF2 substrates by molecular beam epitaxy (MBE), yielding ZT values of 0.4 to 0.8.[3]

A major challenge in magnetron sputtering is stoichiometry control, since the sticking coefficient of Te is significantly smaller than 1 [4] at typical substrate temperatures of about 300℃. In this work, binary Bi_2Te_3 thin films were obtained by a growth concept which allows the problem of stoichiometry control to be overcome. The growth concept is referred to as nano-alloying [5,6]comprising alternate deposition of elemental temperature and subsequent annealing for phase formation.

Experimental Results and Discussion

Bi_2Te_3 has a rhombohedral layered structure with space group R-3m and lattice parameters a=0.4386 nm and c=3.0497 nm for Bi_2Te_3.[7]. For thin film grown by Magnetron Sputtering, (111)-oriented Bi_2Te_3 or commercial Si wafers with 100-nm-thick amorphous SiO_2 on top were used as substrates.

Bi_2Te_3 of 80 nm in thickness are grown on silicon<110> templates. The Bi_2Te_3 concentrations were determined by $\theta/2\theta$ scans of the reflection using x-ray diffraction. Since both silicon samples templates are electrically conductive, we deposited 60 nm SiO_2 on the surfaces of both structures prior to the deposition of line heater/sensor. This layer provides the electrical insulation required for the 3ω measurements. Then, heaters/sensors of identical geometry, composed of Cr (28 nm) □Au (160 nm) with the wire width and length of 16 μm and 1100 μm, respectively, were patterned on the top of the SiO_2 layer of both structures using optical photolithography followed by metal deposition and lift-off techniques. A digital lock-in amplifier was used to feed the sinusoidal current into the specimen at an angular frequency ω and collect the voltage at a frequency 3ω across. Figure 1 is a sample of X-ray diffraction pattern. The XRD results obtained for Bi_2Te_3 films deposited on BaF_2 substrates are shown in Fig. 1. Both as-deposited and annealed Bi_2Te_3 thin films yielded (00l) reflections as well as various (hkl) reflections of the Bi_2Te_3 structure.

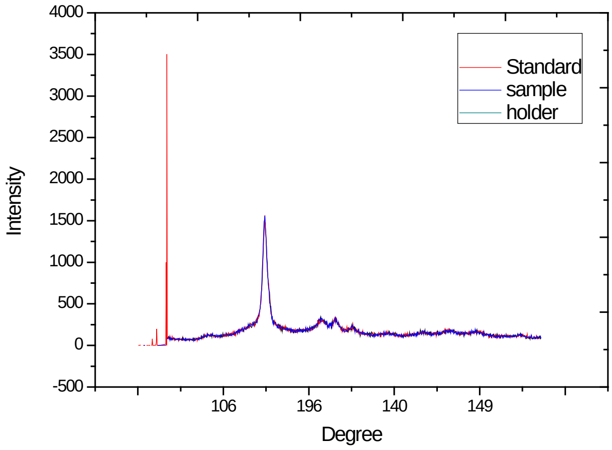

Fig. 1 XRD Results

The microstructure and chemical composition on annealed samples prepared in cross-section were analyzed by analytical TEM. The secondary phases turned out to be Bi-rich with up to 54 at.% Bi and were arranged in layers at Bi2Te3 grain boundaries with thickness of about 10 nm to 20 nm. The Bi-rich grain boundary phases might act as insulating layers, severely reducing the charge carrier mobilities. Finally, Bi2Te3 grains without intermediate Bi-rich layer revealed facetedgrain boundaries with wavelength of 15 nm and amplitude of 9 nm.

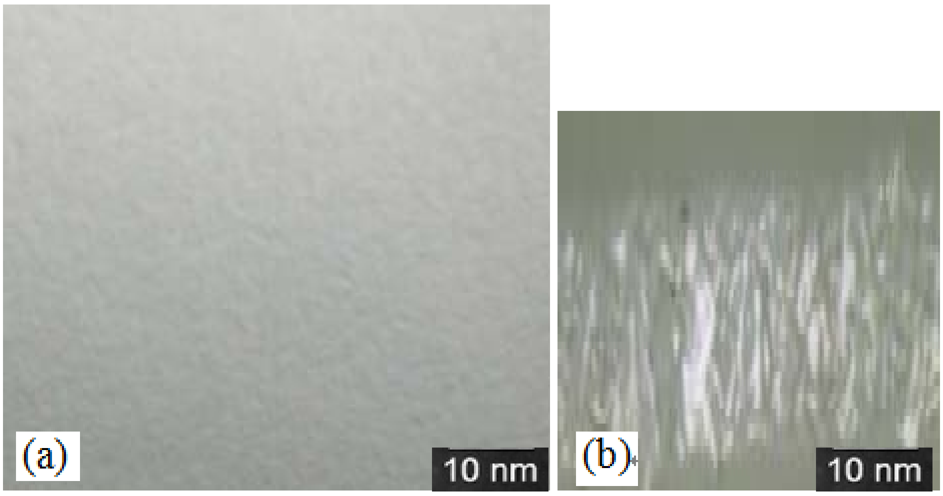

Fig. 2 (a) SEM images (b)Cross-sections images

Summary

The future communicationplatforms will employ highly sophisticatedmicro-nanoscale sensor systems in which III-nitride baseddevices will play increasingly important roles because oftheir superior material properties and the development of III-nitride based TE devices may open up the possibility formonolithic integration of TE power generator/cooler modulesonto remote micro-nanoscale sensor networks.

Nano-alloying combined with subsequent annealing, yielded (i) stoichiometric thin films, (ii) accurate and easy control of Te content, (iii) high-quality layer-by-layer growth, (iv) polycrystalline films with average grains size of 80 nm for Bi_2Te_3 film, and Microstructures and transport properties were very similar for and SiO_2 substrates. Thus, nano-alloying could be a key technology for industrial, large-scale production of thin-film devices. With respect to the transport Fig. 2. bright-field SEM images obtained on cross-sections of nano-alloyed thin films grown on SiO_2 substrates:(a) two grains in Sb_2Te_3 with natural nanostructures (nns), and (b) high-resolution cross-sections images of grain boundaries in Bi_2Te_3 films with and without Bi-rich blocking layer, respectively. Aabdin, Peranio, Winkler, Bessas, Ko¨nig, Hermann, Bo¨ttner, and Eibl properties, thin films synthesized by nano-alloying were competitive with thin films grown by Magnetron Sputtering. Particularly, Sb_2Te_3 films showed high-quality thermoelectric properties due to outstanding charge carrier mobility ($l = 402cm^2\ V^{-1}s^{-1}$) and large power factor ($S2r = 29\mu Wcm^{-1}\ K^{-2}$). In Bi_2Te_3 films, Bi-rich grain boundary phases were identified as the limiting factor for charge carrier mobility ($l=80cm^2\ V^{-1}\ s^{-1}$) and thereby power factor ($S^2r = 8\ \mu W\ cm^{-1}\ K^{-2}$). As compared with bulk materials, after annealing the thin films revealed low charge carrier densities and, surprisingly, n-type character for Bi_2Te_3 films. The low charge carrier densities can be explained by reduced antisite defect density due to the low temperatures to which the thin films were exposed during annealing, i.e., low annealing temperatures of 250℃ as compared with congruent melting temperatures beyond 585℃for bulk materials. Detailed discussion is given elsewhere[8].

Acknowledgments

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