Interfacial Characterization of Cobalt Contacts on Bismuth Selenium Telluride for Thermoelectric Devices

R. P. Gupta,a O. D. Iyore,a K. Xiong,a J. B. White,b Kyeongjae Cho,a,* H. N. Alshareef,a,c and B. E. Gnadea,z

1Department of Material Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, USA
2Marlow Industries Incorporated, a subsidiary of II-VI Incorporated, Dallas, Texas 75238, USA
3Material Science and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955-6900 Saudi Arabia

Thermoelectric (TE) coolers have been extensively used in the optoelectronic, automotive, space, and semiconductor industries where low device operational temperature is a key to the device performance in terms of speed and reliability.1 Plated Ni has been used as a barrier metal between Cu and both p- and n-type bismuth–telluride-based thermoelectrodes. The contact resistivity between plated Ni and Bi2Te3 was measured to be approximately 5 × 10−6 Ω cm2, which is about 1 order of magnitude higher than needed for next generation, small TE coolers.2 A process was developed to reduce the contact resistivity by at least 10 times with sputtered Ni as the contact metal on bulk Bi2Te3. However, while sputtered Ni provides low contact resistivity, it shows significant diffusion into the TE material after annealing at 200°C.3 The Ni diffusion appears to degrade the TE properties of the TE material, resulting in poor cooler performance.3 In this study, we present the interface characterization of sputtered Co on bulk Bi2Te3 and compare the results to sputtered Ni films. The coefficient of thermal expansion of Co matches that of bulk Bi2Te3. CoTe2 is the preferred phase that is formed. First principles calculations for Bi2Te3 support the experimental observation.

Sputtered Co is investigated as a suitable contact metal for bulk Bi2Te3, and the results are compared to sputtered Ni. The coefficient of thermal expansion of Co matches that of bulk Bi2Te3 used in our study, and the compatible interface favors the selection of Co as a contact metal. Significant Ni diffusion into Bi2Te3 was observed. In contrast, Co on Bi2Te3 shows significantly less diffusion, even at anneal temperatures as high as 200°C. CoTe2 is the preferred phase that is formed. First principles calculations for Bi2Te3 support the experimental observation.

Grazing incidence X-ray diffraction (GIXRD) was used for the structural characterization of the as-deposited and annealed films using a Rigaku ULTIMA III system with Cu Kα (λ = 1.54 Å) X-ray radiation operated at 40 kV and 44 mA. GIXRD uses a small incident angle for the incoming X-rays so that the diffraction is surface sensitive, minimizing the contribution from the substrate. A thin film can be probed through its thickness by varying the angle of incidence to obtain depth-resolved information about the structure and the interfaces.4,5 GIXRD revealed the presence of CoTe2 at the interface for the 90 nm sputtered Co film annealed at 200°C for 1 h. No other CoTe3 phases were observed for the as-deposited sample, as seen in Fig. 1. Figure 1 also compares the X-ray diffraction (XRD) pattern for the sputtered Co sample annealed at 200°C in N2 for ω = 0.5, 1, and 2° where ω is the angle of incidence for the X-ray beam. The X-rays penetrate further into the sample as the angle of incidence is increased. No CoTe2 peaks are seen at ω = 0.5°, which suggests that the CoTe2 is not on the film surface but only at the interface. The CoTe2 peaks agree with Borstigen and Kjekshus,6 where the crystal structure for CoTe2 is orthorhombic belonging to the Pmn21 (34) space group with cell dimensions a = 5.3 Å, b = 6.3 Å, and c = 3.9 Å (α = 90°, β = 90°, and γ = 90°) while Co is hexagonal with cell dimensions a = 2.5 Å, b = 2.5 Å, and c = 4.1 Å (α = 90°, β = 90°, and γ = 120°), and space group P63/mmc (194).5 Ko et al. showed that a sputtered Co film deposited at room tem-

Figure 1. XRD spectra for the as-deposited 90 nm sputtered Co film taken at an X-ray incidence angle of ω = 2° and annealed film at 200°C for ω = 0.5, 1.0, and 2.0°.
temperature on Si/H₂O is amorphous and becomes crystalline when annealed at 300°C. The XRD data on as-deposited sputtered Co shows a similar trend and is weakly crystalline. Co is also known to change phase from α-Co (hexagonal close-packed) to β-Co (face-centered cubic) at 380°C. For the TE material that has hexagonal symmetry, α-Co would be preferred. The TEM image in Fig. 2 shows no diffusion for sputtered Co on Bi₂Te₃Se after annealed at 200°C. A sharp interface, on the order of the roughness of the substrate Ra ~ 4 nm, can be observed, which agrees with the GIXRD results.

Figure 3 shows XRD spectra with an X-ray incidence angle of ω = 2° for sputtered Ni films on Bi₂Te₃Se after different annealing temperatures. In contrast to the sputtered Co films, Ni shows strong diffraction peaks indicative of a crystalline structure even for the as-deposited film and NiTe forms at anneal temperatures as low as 100°C. The intensity of the NiTe(101) peak for the sample annealed at 200°C is proportional to the thickness of the NiTe layer that is formed. The cross-sectional TEM image of the same sample shows a 460 nm diffused region, as seen in Fig. 4.

To understand the stability of Ni and Co on bulk Bi₂Te₃Se, we performed first principles calculations on pure Bi₂Te₃ to study Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces using the total energy plane-wave basis code VASP. The calculated enthalpies of the formation of bulk NiTe, CoTe, NiTe₂, and CoTe₂ are 0.4, 0.17, 0.72, and 0.64 eV, respectively, indicating that Ni tellurides are more stable than Co tellurides. The formation energies for incorporating Te and Bi into bulk Co are 1.05 and 2.65 eV, respectively. For comparison, the formation energies for incorporating Te and Bi into bulk Ni are higher than the Co case, are 0.64 and 1.99 eV, respectively. We now consider the Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces. For each metal, two types of interfaces were considered: Bi terminated and Te terminated. The relative stability of these interfaces is determined by calculating their interface formation energies. Figure 5 shows the...
interface formation energy of Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces as a function of Te chemical potential, relative to the formation energy of the Te-terminated Ni/Bi₂Te₃ interface. It shows that for each metal, the Bi-terminated interfaces have lower interface formation energy than the Te-terminated interfaces. More importantly, the formation energies for Co/Bi₂Te₃ interfaces are much lower than Ni/Bi₂Te₃ interfaces by approximately 7 eV. This may explain why Ni interacts more readily with Bi₂Te₃ to form a thick NiTe interfacial region, while Co does not. The formation of the Ni/Bi₂Te₃ interface is less energetically expensive so that Ni tends to diffuse into Bi₂Te₃ to form an interface with lower energy.

In conclusion, we have shown the interfacial reaction of sputtered Co and Ni with bulk Bi₂Te₃ during low temperature anneals. The dominant phases formed were CoTe₂ and NiTe for Co and Ni, respectively. At 200°C Ni tends to diffuse into the substrate, while no such diffusion was observed for Co films. Quantum simulations substantiate this observed diffusion. The simulations show that Co forms a more stable interface with Bi₂Te₃, while Ni tends to diffuse into the substrate to lower its energy state. The minimal diffusion of Co implies that the TE material should not degrade at high device operating temperatures. Work is in progress on measuring contact resistance of sputtered Co on thin-film Bi₂Te₃ after different postanneal temperatures. Initial results show that sputtered Co gives comparable contact resistance to sputtered Ni, while providing a more stable interface.

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