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

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Sputtered Co is investigated as a suitable contact metal for bulk $\text{Bi}_2(\text{Te,Se})_3$, and the results are compared to sputtered Ni. The coefficient of thermal expansion of Co matches that of bulk $\text{Bi}_2(\text{Te,Se})_3$ used in our study, and the compatible interface favors the selection of Co as a contact metal. Significant Ni diffusion into $\text{Bi}_2(\text{Te,Se})_3$ was observed. In contrast, Co on $\text{Bi}_2(\text{Te,Se})_3$ shows significantly less diffusion, even at anneal temperatures as high as 200°C. CoTe_2 is the preferred phase that is formed. First principles calculations for Bi_2Te_3 support the experimental observation.

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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 thermoelements. The contact resistivity between plated Ni and $\text{Bi}_2(\text{Te,Se})_3$ was measured to be approximately $5 \times 10^{-6} \Omega \text{ cm}^2$,² which is about 1 order of magnitude higher than needed for next generation, small TE coolers.³ A process was developed to reduce the contact resistance by at least 10 times with sputtered Ni as the contact metal on bulk $\text{Bi}_2(\text{Te,Se})_3$. However, while sputtered Ni provides low contact resistivity, it shows significant diffusion into the TE material after annealing at 200°C.⁴ The Ni diffusion appears to degrade the TE properties of the TE material, resulting in poor cooler performance.⁵ In this study, we present the interface characterization of sputtered Co on bulk $\text{Bi}_2(\text{Te,Se})_3$ and compare the results to sputtered Ni films. The coefficient of thermal expansion of Co matches that of bulk $\text{Bi}_2(\text{Te,Se})_3$, making it a good candidate for a contact metal.

An AJA ATC Orion 4 HV Magnetron system was used to sputter Ni and Co onto polycrystalline $\text{Bi}_2(\text{Te,Se})_3$. The substrates were rinsed with acetone, isopropyl alcohol, and deionized water before loading in the deposition system. The substrates were sputter-cleaned with Ar^+ in situ before deposition to remove surface contaminants and native oxide. The Co and Ni films were sputtered for 10 and 15 min at room temperature, respectively, at a vacuum pressure of 4 mTorr and a power density of 10 W/cm². The thicknesses obtained for Ni and Co were 120 and 90 nm, respectively, as measured using a cross sectional scanning electron microscopy image.

The interfacial characterization of the samples was carried out using a JEOL 2100F transmission electron microscope (TEM) operated at 200 kV. Cross-sectional specimens for TEM analysis were prepared using a lift-out technique with an FEI Nova 200 dual column focused ion beam (FIB)/scanning electron microscopy system. This technique avoids dimpling difficulties and thermal exposure artifacts of the traditional polishing procedure for this material. A 3 μm thick Pt film was deposited in situ using an organometallic precursor for protection of the Co film during the sample preparation, and FIB polishing parameters were optimized for the soft TE material.

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 K α ($\lambda = 1.54 \text{ \AA}$)

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.^{6,7}

GIXRD revealed the presence of CoTe_2 at the interface for the 90 nm sputtered Co film annealed at 200°C for 1 h. No other Co_xTe_y 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 N_2 for $\omega = 0.5, 1$, 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 CoTe_2 peaks are seen at $\omega = 0.5^\circ$, which suggests that the CoTe_2 is not on the film surface but only at the interface. The CoTe_2 peaks agree with Borstigen and Kjekshus,⁸ where the crystal structure for CoTe_2 is orthorhombic belonging to the $Pnn2$ (34) space group with cell dimensions $a = 5.3 \text{ \AA}$, $b = 6.3 \text{ \AA}$, and $c = 3.9 \text{ \AA}$ ($\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$) while Co is hexagonal with cell dimensions $a = 2.5 \text{ \AA}$, $b = 2.5 \text{ \AA}$, and $c = 4.1 \text{ \AA}$ ($\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 120^\circ$), and space group $P63/mmc$ (194).⁹ 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 $\omega = 2^\circ$ and annealed film at 200°C for $\omega = 0.5, 1.0$, and 2.0° .

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Figure 2. (Color online) (a) TEM image of 90 nm sputtered Co film on Bi_2Te_3 annealed at 200°C . (b) High resolution image of the interface region between Co and Bi_2Te_3 . (c) Lattice image of the Bi_2Te_3 area showing Bi-Te stack lines. (d) Lattice image of the Co region showing the hexagonal crystal atomic sites.

perature on Si(100) is amorphous and becomes crystalline when annealed at 300°C .¹⁰ The XRD data on as-deposited sputtered Co show a similar trend and are weakly crystalline. Co is also known to change phase from α -Co (hexagonal close-packed) to β -Co (face-centered cubic) at 380°C .¹¹ 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 $\text{Bi}_2(\text{Te,Se})_3$ annealed at 200°C . A sharp interface, on the order of the roughness of the substrate $R_a \sim 4$ nm, can be observed, which agrees with the GIXRD results.

Figure 3 shows XRD spectra with an X-ray incidence angle of $\omega = 2^\circ$ for sputtered Ni films on $\text{Bi}_2(\text{Te,Se})_3$ after different annealing temperatures. In contrast to the sputtered Co films, Ni shows

Figure 3. XRD spectra taken at an X-ray incidence angle of $\omega = 2^\circ$ comparing 120 nm sputtered Ni film for as-deposited, 100°C , and 200°C annealed samples.

Figure 4. TEM image of 120 nm sputtered Ni on Bi_2Te_3 annealed at 200°C showing 460 nm of diffused NiTe region.

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 .² 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 $\text{Bi}_2(\text{Te,Se})_3$, we performed first principles calculations on pure Bi_2Te_3 to study Ni/ Bi_2Te_3 and Co/ Bi_2Te_3 interfaces using the total energy plane-wave basis code VASP.¹² The calculated enthalpies of the formation of bulk NiTe, CoTe, NiTe_2 , and CoTe_2 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/ Bi_2Te_3 and Co/ Bi_2Te_3 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

Figure 5. (Color online) Quantum simulation result showing interface formation energy of various interfaces as a function of Te chemical potential.

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.¹³ 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 Bi₂(Te,Se)₃ 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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