Highly Effective GeNi Alloy Contact Diffusion Barrier for BiSbTe Long-Term Thermal Exposure

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ABSTRACT: A GeNi alloy diffusion barrier for contacts on bismuth antimony telluride is proposed. Multiple gold contact diffusion barriers were tested at different thermal aging conditions in air and reducing atmospheres. Among all diffusion barriers, the GeNi alloy barrier shows the best performance for bulk samples with no substantial degradation of the contact resistance, no contact color change, and no change of thermoelectric properties. We observed $D_{Au-GeNi} = (9.8 \pm 2.7) \times 10^{-20} \text{m}^2/\text{s}$ within the GeNi alloy barrier, which is 4 times smaller than $D_{Au-BiSbTe}$. The presence of the initial Ge layer also proves to be effective in reducing nickel diffusion yielding $D_{Ni-BiSbTe} = (8.57 \pm 0.49) \times 10^{-19} \text{m}^2/\text{s}$. During GeNi alloy formation, Ge diffusion into BiSbTe produces GeTe, which apparently blocks the van der Waals gaps eliminating Au and Ni fast diffusion pathways. Thermal aging of BiSbTe nanowires shows that Au and Ni diffusion degrades the thermoelectric power factor, whereas the GeNi alloy barrier sample is mostly preserved. The GeNi alloy barrier is a reliable solution to long-term thermal applications of BiTe-based materials.

INTRODUCTION

BiTe- and BiSe-based materials have a unique crystal structure with large spacing between the group VIA (Te or Se) atoms along the c-axis direction because of bonding by relatively weak van der Waals forces. Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_2$Sb$_2$-Te$_3$ are examples of group V-IVA materials containing van der Waals gaps. These materials are known as topological insulators with great potential for thermoelectric applications. The stability and performance of electrical and thermal contacts for long-term thermoelectric applications are one of the most important topics for research and industrial devices. Gold is a desirable metal contact because of its chemical inertness and high electrical and thermal conductivities. However, a large contact resistivity ($\sim 10^{-8}$ to $10^{-9} \Omega \text{m}^2$) between Au and BiTe-based materials is reported. This limitation is also observed for other common metal contacts such as Ag and Cu.

In addition, these metals diffuse along the direction of the van der Waals gaps limiting high temperature or thermal contact annealing applications. Although Au solubility in BiTe-based materials is low, its fast diffusion causes material loss, resulting in contact degradation proportional to the operating temperature. BiSbTe and BiTe-based thermoelectric devices operating at such a high temperature must have insignificant contact diffusion to be reliable in long-term applications. Contact diffusion barriers such as nickel and cobalt have been employed to prevent Au diffusion, but they are still permeable to Au, resulting in contact material loss and electrical contact degradation. In fact, Ni strongly diffuses into BiTe-based materials, so it is not a desirable choice for long-term high-temperature thermoelectric applications. In this work, a GeNi alloy barrier for Au contacts on BiSbTe is explored. We found that the GeNi alloy barrier does not alter the electrical contact characteristics and it preserves the contact appearance even after long-term thermal aging studies.

Experimental Methods. The electrical contact resistance for bulk samples was evaluated by the transfer length method (Figure 1A). E-beam contact evaporation through a shadow mask was employed to make electrical contacts on Bi$_{0.5}$Sb$_{1.5}$Te$_3$ bulk polycrystalline samples. The diffusion barrier test was carried out by first evaporating the barrier material, immediately followed by 1000 nm Au evaporation. Ni (100 nm), W (100 nm), Ge (100 nm), or Ge (80 nm)/Ni (100 nm) were tested as diffusion barriers. The Ge/Ni barrier was rapid thermal annealed (RTA) at 350 °C for 3 min in forming gas in...
order to produce a germanium–nickel alloy (GeNi). The resistances of the samples were measured right after contact deposition (the GeNi/Au sample was annealed at 350 °C for 3 min before resistance measurement) and kept at ambient conditions for 5 days. After that period, bulk samples were tested before and after thermal aging at 250 °C in forming gas (N₂ 95%, H₂ 5%) up to 5 h, or at 200 °C in air up to 2 weeks. The 5 day waiting period ensured that any contact resistivity change after thermal aging is the result of material diffusion rather than contact degradation due to ambient exposure. Energy-dispersive system (EDS) was carried out on an FEI dual-beam focused ion beam/scanning electron microscope and the atomic ratios were analyzed by EDAX genesis software.

Figure 1. (A) Optical image of a Bi₀.₅Sb₁.₅Te₃ bulk sample with Au contact pads. Inset: Representation of the transfer length characterization. (B) SEM image of the NW thermoelectric characterization platform. Right inset: BiSbTe NW with Ge/Ni/Au contacts. Left inset: Illustration of the top contact fabrication procedure. (C) EDS spectrum of bulk Bi₀.₅Sb₁.₅Te₃ sample. The Si, Na, Al, and K peaks are from glass substrate. (D) Resistances vs contact separation length for Bi₀.₅Sb₁.₅Te₃/Au samples before and after thermal aging in forming gas at 250 °C for 5 h. Solid lines represent the linear fitting of the data.

For BiSbTe nanowires (NWs), we measured 4-probe electrical resistivity, contact resistivity, and Seebeck coefficient from 25 to 310 K to evaluate the influence of thermal aging for Au, Ni/Au, and GeNi/Au contacts. The theromolectric measurement platform was patterned by a combination of photo- and electron-beam lithographies on a ⟨100⟩ silicon wafer with 1 μm thermal silicon dioxide on the surface. Contacts were patterned on the substrate by photolithography followed by the sequential deposition of 5 nm Cr and 50 nm Au. An e-beam lithography (EBL) procedure was carried out to pattern a thin line perpendicularly crossing the bottom contact lines of about 400 nm wide and 23 μm long for BiSbTe NW evaporation. After e-beam resist development, oxygen plasma at 30 W for 3 min was carried out, and the exposed gold contacts at the patterned regions were etched with I₂/KI aqueous solution for 20 s (Figure 1B left inset) followed by deionized (DI) water rinse. Then, the sample was exposed to 1:6 buffered oxide etch solution for 10 s followed by DI water rinse. The sample was placed in a thermal evaporation unit to deposit about 300 nm BiSbTe from Bi₀.₅Sb₁.₅Te₃ source material. After lift-off in acetone, a second EBL step was carried out again to pattern the four top contact lines on the NW (Figure 1B left inset, yellow lines). The following metal recipes were e-beam evaporated for the top contacts: 5 nm Cr (adhesion layer)/300 nm Au (referred to as Au contact sample), 100 nm Ni/250 nm Au, or 80 nm Ge/100 nm Ni/250 nm Au. The thermally evaporated BiSbTe NW has an elemental composition of Bi (8.84%), Sb (61.38%), and Te (29.78%) (Figure 1C). These NW devices were thermally aged under vacuum in forming gas (N₂ 95%, H₂ 5%) for various lengths of time.

The thermal and electronic properties of the samples were measured from 25 to 310 K in a helium closed-loop cryostat. The electrical resistivity, ρ, was calculated from 4-probe resistance data at each temperature using the dimensions (cross-sectional area and length) measured by SEM. The Seebeck coefficient (S = −ΔVth/ΔT) was extracted by measuring ΔVth when a dc current was applied on the heater producing a temperature gradient ΔT between the two middle contacts. Electrical contacts were confirmed to be Ohmic for Ni/Au and GeNi/Au contact samples within the entire temperature range while the Au contact sample was not Ohmic below 140 K. Measurements were taken on the same sample before and after thermal aging to determine the changes caused by contact diffusion.
Contact Thermal Aging Studies for Bulk Samples.

Bi$_{0.5}$Sb$_{1.5}$Te$_3$ resistances for bulk devices are shown in Figure 1D for samples before and after thermal aging. After thermal aging, the slope of the linear regression does not appreciably change, indicating that the resistance of bulk Bi$_{0.5}$Sb$_{1.5}$Te$_3$ is not affected. However, the intercepts are different because of a change of contact resistance. Au diffuses into the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ crystal matrix through the van der Waals gaps during thermal aging. A consequence of Au diffusion into the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ material is electrical contact degradation, and contact and substrate color change. The contact resistivity for Bi$_{0.5}$Sb$_{1.5}$Te$_3$/Au bulk sample increased from $(3.39 \pm 0.17) \times 10^{-9}$ to $(4.88 \pm 0.91) \times 10^{-9}$ Ω m$^2$ after thermal aging (Table 1). During RTA, GeNi is formed in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$/Ge/Ni/Au system (Table 1, Figures 2 and 3E). The Ni/Au and the Ge/Au diode contacts.38 The diffusion of Au in Ge is considered relatively slow.42 The diffusion length calculated by $2 \sqrt{D_{\text{Au-Ge}}t}$ (where $D_{\text{Au-Ge}}$ is diffusion coeff. of Au in Ge, t = time) is ca. 13 nm after thermal aging assuming $D_{\text{Au-Ge}} = 1.6 \times 10^{-21}$ m$^2$/s.42 Thus, the Ge layer acted as an effective diffusion barrier for Au, but it is not practical for thermoelectric applications.

Table 1 also shows the contact resistivity for several barrier recipes before and after thermal aging in forming gas at 250 °C for 5 h. The Ni/Au sample data yielded a smaller slope after thermal aging (Figure 2) because of a decrease of bulk electrical conductivity, and it is commonly used for Schottky diode contacts.38–41 The diffusion of Au in Ge is considered relatively slow.42 The diffusion length calculated by $2 \sqrt{D_{\text{Au-Ge}}t}$ (where $D_{\text{Au-Ge}}$ is diffusion coeff. of Au in Ge, t = time) is ca. 13 nm after thermal aging assuming $D_{\text{Au-Ge}} = 1.6 \times 10^{-21}$ m$^2$/s.42 Thus, the Ge layer acted as an effective diffusion barrier for Au, but it is not practical for thermoelectric applications.

Among all samples subjected to thermal aging, the GeNi/Au contact showed an insignificant increase of electrical contact resistivity, no apparent contact color change, and no appreciable degradation of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ bulk resistance (Table 1, Figures 2 and 3E). The Ni/Au and the Ge/Au contacts do not perform as well as the GeNi/Au contact. During RTA, GeNi is formed in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$/Ge/Ni/Au sample.30 The GeNi layer is expected to have a relatively low electrical resistivity. A contact resistivity of about $2 \times 10^{-11}$ Ω m$^2$ for a GeNi contact on n-type Ge substrate was reported.34 We conclude that the initial RTA step for the Bi$_{0.5}$Sb$_{1.5}$Te$_3$/Ge/Ni/Au sample is fundamental for achieving a small contact resistivity.

During thermal aging, the GeNi barrier restricted the Au diffusion into bulk Bi$_{0.5}$Sb$_{1.5}$Te$_3$ based on the results shown in Figures 2 and 3. The concentration depth profiles measured by EDS after thermal aging for Au and GeNi/Au contacts on thermal evaporated BiSbTe samples are shown in Figure 4. Au diffusion reached about 600 nm without the GeNi barrier (Figure 4A). Assuming that the EDS intensity (I) is directly proportional to the concentration, the diffusion coeff. of Au in BiSbTe can be found by $I(x,t) = (I_0 - I_w)/(I_0 - I_w) = erfc(x/4.41 \times 10^{-21} m^2/s)$ at time t = 5 h.

Table 1. Contact Resistivities before and after Thermal Aging at 250 °C in Forming Gas

| contact       | before aging (10$^{-9}$ Ω m$^2$) | after aging (10$^{-9}$ Ω m$^2$) | color change |
|---------------|----------------------------------|---------------------------------|--------------|
| Au            | 3.39 ± 0.17                      | 4.88 ± 0.91                     | yes          |
| Ni/Au         | 3.70 ± 0.94                      | 3.47 ± 0.28                     | yes          |
| W/Au          | ≈150                             | ≈96                             | yes          |
| Ge/Au         | not conductive                   | not conductive                  | yes          |
| GeNi/Au       | 3.30 ± 0.89                      | 3.44 ± 0.45                     | no           |

“Standard deviations: ± 95.5% confidence interval.”

Figure 2. Resistances for Bi$_{0.5}$Sb$_{1.5}$Te$_3$/GeNi/Au and Bi$_{0.5}$Sb$_{1.5}$Te$_3$/Ni/Au samples before and after thermal aging in forming gas at 250 °C for 5 h.

Figure 3. Au discoloration after thermal aging at 250 °C for 5 h in forming gas. (A) Ge/Ni before thermal aging. (B) No barrier. (C) 100 nm Ni. (D) 100 nm Ge. (E) 80 nm Ge/100 nm Ni. All the devices before thermal aging had the same Au contact color appearance.

Figure 4. EDS depth profiles for Au and GeNi on GeNi/Au and Ge/Ni/Au contacts on Bi$_{0.5}$Sb$_{1.5}$Te$_3$.
On the basis of the Au EDS profile shown in Figure 4B, L is observed to be ca. 125 nm, so \(D_{\text{Au-GeNi}} = (9.8 \pm 2.7) \times 10^{-20} \text{ m}^2/\text{s} \) was obtained, assuming that \(D_{\text{Au-BiSbTe}}\) remained the same as observed in Figure 4A. It seems that the initial RTA step resulted in a substantial diffusion of Au into the entire sample while the GeNi layer was produced. During thermal aging, the slower diffusion of Au in the GeNi layer reduces the amount of Au diffusing into the BiSbTe.

\[
(I(x, t) - I_\infty) = \frac{(I_s - I_\infty)\gamma}{\sqrt{4\pi D t}} \exp \left(-\frac{x^2}{4D t}\right)
\]

(2)

From Figure 2, nickel diffusion in BiSbTe/GeNi/Au seems insignificant because the contact resistance did not decrease and the overall resistance of bulk BiSbTe did not change as observed for the BiSbTe/Ni/Au sample. No appreciable Ni is observed beyond ca. 200 nm from the BiSbTe/GeNi/Au interface (Figure 4B). Ni diffusion in the BiSbTe can be modeled by the Gaussian drive-in diffusion equation (eq 2), where \(\gamma\) is a fitting constant. \(D_{\text{Ni-BiSbTe}} = (8.57 \pm 0.49) \times 10^{-19} \text{ m}^2/\text{s} \) was obtained from eq 2, which is about 20 times smaller than the previously reported \(D_{\text{Ni-BiSbTe}}\) value.\(^{30}\) GeTe alloy can be produced in situ during RTA.\(^{31}\) Unlike BiTe-based materials, there are no van der Waals gaps between the Te planes in GeTe, thus Ge-rich bismuth telluride materials should have a similar crystalline structure.\(^{32}\) GeTe could have formed at the interface of Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\)/GeNi closing the van der Waals gaps along the [001] direction and preventing a path for the fast diffusion of Au and Ni.

Long-term thermal aging studies carried out in air revealed that the GeNi barrier is also effective in avoiding contact discoloration and contact resistivity degradation (Figure 5). The GeNi barrier is further tested for nanoscale thermoelectric devices. Nanoscale devices should magnify any change of the thermoelectric properties because contact diffusion would occur in a relatively large portion of the BiSbTe NW. Thus, the influence of contact diffusion in BiSbTe NW could be measured in a substantially shorter time compared to the one for bulk samples.

**Contact Thermal Aging Studies for Nanometer-Scale Devices.** To better understand the influence of Au diffusion and the performance of Ni and GeNi barriers on contact thermal aging, studies on NW devices were carried out. Figure 6A shows the 4-probe resistance of the BiSbTe NW samples. None of the samples have electrical contact before annealing. The GeNi/Au sample achieved Ohmic contact after RTA (3 min. at 350 °C) because of the formation of GeNi alloy\(^{35-49}\) while the Ni/Au and Au contact samples achieve Ohmic contacts only after 1 h of thermal aging in forming gas at 250 °C. Au and Ni/Au contacts absorbed into the BiSbTe NW if annealed at 350 °C for 3 min in forming gas. This observation supports the fact that GeNi alloy is a superior diffusion barrier for Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\).

The contact resistivity of GeNi/Au and Ni/Au contacts are more than 3 orders of magnitude lower than the one for Au contact (Figure 6B). The contact resistivity of the Ni/Au sample decreased from 1 to 8 h thermal aging conditions. On the other hand, the contact resistivity of the GeNi/Au sample does not present any detectable change after the first annealing. The Au sample after 1 h of annealing has the largest electrical resistivity, so Au diffusion not only degraded the contact but also negatively influenced the electrical conduction of the NW. By comparing 1–8 h thermal aging,
the resistivity of NW for the Ni/Au device increased about 10% while the resistivity of NW for the GeNi/Au device has no significant change. It is reasonable to assume that the contact metal diffusion in Ni/Au degraded the NW, resulting in an increased 4-probe resistivity. For GeNi/Au sample, the electrical resistivity of the NW increased after 1 h aging, but it remained essentially the same after 8 h of aging. Au diffusion into the NW could degrade the electrical conductivity of the NWs for both Ni/Au and GeNi/Au. However, the fact that after 1 h aging the 4-probe resistance did not change for the GeNi/Au sample implies that the NW degradation process should have stopped.

The Seebeck coefficient versus temperature (Figure 7) shows the dependences of the three samples at the different aging conditions. The Seebeck coefficient at 300 K of the Ni/Au sample decreased nearly 60% after 8 h of thermal aging while the GeNi/Au sample has almost the same Seebeck coefficient. The Seebeck coefficient peaks at about 100 K for the GeNi/Au sample annealed for 3 min at 350 °C in forming gas. This peak is associated with the presence of a small band gap conduction channel in the BiSbTe NW, and it is reduced after thermal aging for the other GeNi/Au samples. The surface states in BiTe-based materials are influenced by doping.\textsuperscript{50} Our BiSbTe NWs are Te depleted, which may have different surface state bands and unpredictable influence on Seebeck coefficient, especially at lower temperature.

At 300 K, the power factor \((S^2/\rho)\) shows a clear trend between metal diffusion and thermal aging (Table 2). Contact metal doping could create centers that quench charges and degrade both electrical conductivity and Seebeck coefficient. The power factor drastically decreased for the Ni/Au sample after 8 h of thermal aging while \(S^2/\rho\) for GeNi/Au sample is nearly constant (Table 2). \(ZT\) is one of the lead parameters associated with the performance of thermoelectric materials.

| Table 2. Power Factor \((S^2/\rho)\, \mu W m^{-1} K^{-2}\) at 300 K as a Function of Thermal Aging Time in Forming Gas |
|---|---|---|---|
| contact | initial | 1 h | 8 h |
| Au | no contact | 33.6 |
| Ni/Au | no contact | 144.1 | 21.8 |
| GeNi/Au | 87.1 | 71.0 | 64.7 |
ZT is directly proportional to $S^2/\rho$ and inversely proportional to the thermal conductivity ($k$). The small $k$ values reported for BiTe-based materials are mainly dictated by phonon scattering at the van der Waals gaps.\(^1\)–\(^3\) Au and Ni diffusions in Bi$_2$SbTe/GeNi/Au are greatly reduced by the formation of GeTe at the Bi$_2$SbTe/GeNi interface resulting in the blocking of van der Waals gaps close to the interface (Figure 4B). Thus, the thermal conductivity for the Bi$_2$SbTe should remain unchanged because of the preservation of bulk van der Waals gaps.

**CONCLUSIONS**

Contact degradation of Bi$_2$SbTe-based materials is observed due to the diffusion of Au. In Bi$_2$SbTe NWs, the diffusion of Au contacts caused a degradation of thermoelectric properties. Ni/Au forms Ohmic contact with small contact resistivity, but Ni is not a diffusion barrier to prevent Au diffusion during long-term thermal aging. For Ni/Au contacts, the electrical resistivity and Seebeck coefficient decrease because of Ni diffusion into the bulk Bi$_2$SbTe. Ge/Ni/Au contact becomes Ohmic after short thermal annealing because of the formation of GeNi alloy. We observed that the GeNi layer prevents Au and Ni diffusion into the Bi$_2$SbTe. We suspect that the formation of GeTe at the Bi$_2$SbTe/Ge interface blocks the van der Waals gaps limiting contact diffusion. Our studies on Bi$_2$SbTe NWs show that GeNi alloy preserves the NW electrical resistivity and Seebeck coefficient, hence it is a superior option for high-temperature operations.

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Notes
The authors declare no competing financial interest. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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