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Electronic structures and stability of Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces

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Abstract
We investigate the electronic structures and stability for Ni/Bi₂Te₃, NiTe/Bi₂Te₃, Co/Bi₂Te₃ and CoTe₂/Bi₂Te₃ interfaces by first-principles calculations. It is found that the surface termination strongly affects the band alignment. Ni and Co are found to form Ohmic contacts to Bi₂Te₃. The interface formation energy for Co/Bi₂Te₃ interfaces is much lower than that of Ni/Bi₂Te₃ interfaces. Furthermore, we found that NiTe on Bi₂Te₃ is more stable than Ni, while the formation energies for Co and CoTe₂ on Bi₂Te₃ are comparable.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The solid-state thermoelectric (TE) cooler is of considerable interest in many applications because of its advantages of reliability, low-noise operation, miniaturization and high power density [1–4]. Commercial TE cooling devices use doped Bi₂Te₃ ((Bi,Sb)₂Te₃ for n-type and Bi₂(Te,Se)₃ for p-type) as the semiconductor material due to its high figure of merit (ZT ∼ 1) [5]. For TE coolers to meet the demands of the industry in terms of high cooling power density, the size of the device needs to be scaled down. Consequently, the electrical resistance between the contact metal and the TE material plays an important role in the device performance [6] since the material ‘figure of merit’ (Z) is degraded by the contact resistance and the relationship between Z and ZD (device figure of merit) can be shown in the following equation:

\[ Z_D = \left( \frac{L}{L + 2r_c \sigma} \right) Z, \] (1)

where \( L \) is the device length, \( r_c \) is the contact resistance and \( \sigma \) is the bulk conductivity. For current bulk TE devices, electroless Ni is used as the contact metal, providing a contact resistance of \( \sim 5 \times 10^{-6} \Omega \text{cm}^2 \) [7]. The contact resistance needs to be at least 10–100 times lower in order to maintain the device scaling [8]. Thus, it is necessary to lower \( r_c \) by engineering the interface between the contact metal and TE materials. The contact resistance of an Ohmic contact depends not only on the contact metal but also on the interfacial reactions. Furthermore, because Bi₂Te₃ has a small band gap of \( \sim 0.16 \text{eV} \) [9], theoretically speaking, it is possible to achieve a much lower contact resistance than is available with electroless Ni.

Recently, we experimentally investigated the Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces with the goal of decreasing the contact resistance. Ni and Co films were sputtered onto polycrystalline bulk Bi₂Te₃ (Se doped) with thicknesses of 120 nm and 90 nm, respectively. After post-annealing the samples at 200 °C in vacuum, we observed a 460 nm NiTe interfacial region for the Ni/Bi₂Te₃ interface [10], while for the Co/Bi₂Te₃ we observed a very thin interfacial region (\( \sim 20 \text{nm} \)) and a small amount of CoTe₂. These results are evident in the XRD spectra (figure 1) and in the cross-sectional TEM images (not shown). The formation of a thick NiTe interfacial region is consistent with previous experimental work [11]. More importantly, the experimentally determined I–V curves of Ni on Bi₂Te₃ show a linear characteristic indicative of an Ohmic contact. This has motivated us to assess the electronic...
structures and stability of Ni/Bi$_2$Te$_3$, Co/Bi$_2$Te$_3$ and related interfaces at an atomic level by first-principles calculations. In this study, we focus on investigating ideal abrupt interfaces that are free of defects and interfacial layers, as we want to determine what the intrinsic properties of these interfaces could be under ideal conditions and compare these with experimental observation.

2. The computational method and model

We performed the calculations using density functional theory with the plane-wave basis code VASP [12]. The exchange correlation energy is approximated by the generalized gradient approximation (GGA). The pseudopotential is described by the projected augmented wave (PAW) method. A $6 \times 6 \times 1$ k-point Monkhorst–Pack grid was sufficient for calculating total energies and a $10 \times 10 \times 1$ grid for the density of states (DOS). We include the spin-polarized and spin–orbit coupling (SOC) effects in our calculations, as they strongly affect the electronic structure of Ni (or Co) and Bi$_2$Te$_3$.

The interfaces are modelled by a superlattice containing one interface and 10 Å vacuum on top. To choose the appropriate metal surface, we can either use the experimental observation by constructing a large lattice-matched superlattice or find a suitable orientation that could give a reasonable cell size. The latter method has been adopted as a compromise between the computational cost and accuracy. We consider Ni(1 1 1), Co(1 1 1), NiTe(0 0 1) and CoTe$_2$(0 1 0) on top of Bi$_2$Te$_3$(0 0 0 1). The metal is compressed or expanded in-plane lattice constants and all angles are kept fixed.

3. Results and discussion

The calculated lattice parameters for bulk Bi$_2$Te$_3$ are $a = 10.6$ Å and $\theta = 24.13^\circ$, in good agreement with the experimental values [13]. The calculated band structure of Bi$_2$Te$_3$ is shown in figure 2. Without including the SOC, we obtained a band gap of 0.33 eV (figure 2(a)). Both conduction band minimum (CBM) and valence band maximum (VBM) are found to lie at $\Gamma$. The SOC effect scales down the band gap to 0.13 eV (figure 2(b)), less than the experimental gap of 0.16 eV due to the well-known LDA error, in good agreement with other theoretical results [9, 14–18]. The CBM and VBM now locate at a point between $Z$ and $\Gamma$. The calculated partial DOS (figures 2(c) and (d)) show that the conduction band (CB) consists mostly of Bi 6p states while the valence band (VB) consists mostly of Te 5p states but there is hybridization between these states, which indicates the covalent Bi–Te interaction. For the metals we used face-centred cubic (fcc) Ni and Co in our calculations. NiTe has a hexagonal structure (P6$_3$/mmc) and CoTe$_2$ has a cubic pyrite structure (Pmn). Our DOS calculations reveal that they both are metallic, consistent with other work [19, 20]. The calculated lattice constants for these metals are also consistent with the experimental data.

To determine the relative stability of these metal/Bi$_2$Te$_3$ interfaces, we calculated their interface formation energies. This is a function of chemical potentials and can be written as [21]

$$E_{\text{form}} = E_{\text{metal}/\text{Bi}_2\text{Te}_3} - nE_{\text{metal}} - \frac{m}{2}E_{\text{Bi}_2\text{Te}_3} - l\mu_{\text{Te}},$$

where $E_{\text{metal}/\text{Bi}_2\text{Te}_3}$ is the total energy of the given supercell, $n$ and $m$ are the number of atoms of metal and Bi, respectively, $E_{\text{Bi}_2\text{Te}_3}$ and $E_{\text{metal}}$ are the total energies per formula unit in Bi$_2$Te$_3$ and the metal, respectively, $l$ is the number of excess (or deficient) Te atoms. There is a single independent parameter determined by the growth conditions, the Te chemical potential $\mu_{\text{Te}}$. Its highest (the least negative) value is $\mu_{\text{Te}}^\text{bulk}$, the energy of bulk Te chemical potential. Its lowest (the most negative) value is for thermodynamic equilibrium with Bi$_2$Te$_3$. Taking the formation enthalpy of bulk Bi$_2$Te$_3$ as $\Delta H \sim -1.3$ eV [23], the limiting values of $\mu_{\text{Te}}$ are $\mu_{\text{Te}} = \mu_{\text{Te}}^\text{bulk} + (\Delta H/3)$ (Bi-rich, favouring Te substitutions) and $\mu_{\text{Te}} = \mu_{\text{Te}}^\text{bulk}$ (Te-rich, favouring Bi substitutions).
Figure 2. Calculated band structure and DOS of bulk Bi$_2$Te$_3$. (a) Band structure without considering SOC, (b) band structure with SOC, (c) partial DOS without SOC and (d) partial DOS with SOC.

Figure 3. Interface formation energies of various interfaces versus Te chemical potential relative to the Te-terminated Ni/Bi$_2$Te$_3$ interface. Solid lines correspond to the formation energies of Ni(Co)/Bi$_2$Te$_3$ interfaces. Dashed lines correspond to the formation energies of NiTe/Bi$_2$Te$_3$ interfaces. Dotted lines correspond to the formation energies of CoTe$_2$/Bi$_2$Te$_3$ interfaces.

Figure 3 shows the interface formation energy for the various interfaces as a function of the tellurium chemical potential $\mu_{Te}$. For Ni (or Co) on Bi$_2$Te$_3$, the formation energy of the Bi-terminated interface increases with increasing $\mu_{Te}$, while the energy of the Te-terminated interface is independent of $\mu_{Te}$. The Bi-terminated interface is always more stable than the Te-terminated interface. More importantly, the formation energies for Co/Bi$_2$Te$_3$ interfaces are much lower than Ni/Bi$_2$Te$_3$ interfaces, by $\sim$7 eV per formula unit. This result may explain why Ni interacts more readily with Bi$_2$Te$_3$ to form a thick NiTe interfacial region while Co does not. On the other hand, the most stable NiTe/Bi$_2$Te$_3$ interface, the Ni–Bi interface, has lower formation energy than the Ni/Bi$_2$Te$_3$ interfaces for all $\mu_{Te}$. This finding is consistent with the experimental fact that NiTe is more stable on Bi$_2$Te$_3$ than Ni. In contrast, the most stable CoTe$_2$/Bi$_2$Te$_3$ interface, the Co–Bi interface, has lower formation energy than Co/Bi$_2$Te$_3$ interfaces only at $\mu_{Te} = -0.32$ eV or below. Above $\mu_{Te} = -0.32$ eV, the Bi-terminated Co/Bi$_2$Te$_3$ interfaced is the most energetically favourable.

Figures 4(a) and (b) show the relaxed structures for Bi-terminated and Te-terminated Ni/Bi$_2$Te$_3$ interfaces. The interfaces are formed by either Ni–Bi or Ni–Te bonds. Each interfacial Bi (or Te) atom is 6-fold coordinated and found to form three bonds with interfacial Ni atoms, as compared with the coordination of their bulk atoms. Co/Bi$_2$Te$_3$ interfaces have similar interfacial bonding, as Co has similar lattice constants as compared with Ni. Figures 4(c) and (d) are the relaxed structures for the most stable NiTe/Bi$_2$Te$_3$ (Ni–Bi) and CoTe$_2$/Bi$_2$Te$_3$ (Co–Bi) interfaces. For the Ni–Bi interface, the interface is formed by Ni–Bi bonds and the interfacial Bi is 4-fold coordinated. The Co–Bi interface is terminated by Co–Bi and Te–Bi bonds, due to the more complicated interface geometry.

Figure 5 shows the spin-resolved and projected DOS of various interfaces without including the SOC effect. The energy of the Fermi level is at zero. It shows that the DOS on atoms well away from the interface (see ‘Bi bulk’ and ‘Te bulk’) replicate those of bulk atoms, as there are no metal states in the Bi$_2$Te$_3$ band gap ($E_g \sim 0.5$ eV), while the DOS of
Figure 4. The interface region of the relaxed atomic structures for (a) Bi-terminated Ni/Bi\textsubscript{2}Te\textsubscript{3}, (b) Te-terminated Ni/Bi\textsubscript{2}Te\textsubscript{3}, (c) Ni–Bi NiTe/Bi\textsubscript{2}Te\textsubscript{3} and (d) Co–Bi CoTe\textsubscript{2}/Bi\textsubscript{2}Te\textsubscript{3} interfaces. Bi: large spheres; Te: medium spheres; Ni: small gray spheres; Co: small black spheres.

interfacial atoms (see ‘Bi interface’ and ‘Te interface’) show the expected tailing of metal states into the Bi\textsubscript{2}Te\textsubscript{3} band gap. Moreover, it reveals that Ni and Co prefer to be in a magnetic state, while Bi and Te away from the interface do not have any magnetization effects. The position of the Fermi level depends on the interfacial bonding configuration. For Bi-terminated interfaces the Fermi level lies close to the VB edge, while for Te-terminated interfaces the Fermi level lies ∼0.3 eV above the VB edge, close to the CB.

Figure 6 shows the projected DOS of these interfaces when including the SOC effect. The SOC effect scales the band gap down to ∼0.1 eV. Since the SOC mainly lowers the energies of the CB of Bi\textsubscript{2}Te\textsubscript{3} (Bi p bands), for the Bi-terminated interfaces the Fermi level still locates at the VB edge, but for the Te-terminated interfaces it now lies at the CB edge.

The p-type Schottky barrier heights, Φ\textsubscript{p}, of these interfaces are evaluated by the so-called ‘bulk plus lineup’ method [23], which is expressed as

$$\Phi_p = \Delta E_{\text{bulk}} + \Delta V_{\text{interface}},$$

(3)

where Δ\textsubscript{E_{bulk}} is the energy difference from the Fermi energy of the metal and the Bi\textsubscript{2}Te\textsubscript{3} VB top, which are obtained from bulk calculations and the energies are referenced with respect to their bulk electrostatic potentials. Δ\textsubscript{V_{interface}} is the shift in the electrostatic potential across the interface from metal (denoted as V\textsubscript{Ni}) to Bi\textsubscript{2}Te\textsubscript{3} (denoted as V\textsubscript{Bi\textsubscript{2}Te\textsubscript{3}}), which is obtained from the supercell calculation by assuming that the potential far enough from the interface is analogous to the bulk potential.

Figure 7 shows the calculated planar-averaged potentials along the z-direction of Bi- and Te-terminated Ni/Bi\textsubscript{2}Te\textsubscript{3} interfaces. To evaluate Δ\textsubscript{V_{interface}} two regions away from the interface were selected for extracting the reference potentials of Ni (from 0 to 4 Å) and Bi\textsubscript{2}Te\textsubscript{3} (from 27.26 to 34.70 Å and from 29.10 to 39.61 Å for Bi- and Te-terminated interfaces, respectively) [24]. In figure 7 the magnitudes of (E\textsubscript{F} − V\textsubscript{Ni}) and (E\textsubscript{Bi\textsubscript{2}Te\textsubscript{3}} − V\textsubscript{Bi\textsubscript{2}Te\textsubscript{3}}) are almost the same as those in bulk calculations, which are ∼4.7 eV and 6.45 eV, respectively, indicating that the supercell is large enough.

The calculated Φ\textsubscript{p} for Bi-terminated Ni/Bi\textsubscript{2}Te\textsubscript{3} and Co/Bi\textsubscript{2}Te\textsubscript{3} interfaces are −0.1 eV and −0.17 eV, respectively. This means that for Bi-terminated Ni/Bi\textsubscript{2}Te\textsubscript{3} and Co/Bi\textsubscript{2}Te\textsubscript{3} interfaces, the Fermi level lies below the Bi\textsubscript{2}Te\textsubscript{3} VB edge so...
Figure 5. The spin-resolved and projected partial DOS of (a) Bi-terminated and (b) Te-terminated Ni/Bi$_2$Te$_3$ interfaces, (c) Bi-terminated and (d) Te-terminated Co/Bi$_2$Te$_3$ interfaces, (e) Ni–Bi NiTe/Bi$_2$Te$_3$ and (f) Co–Bi CoTe$_2$/Bi$_2$Te$_3$ interfaces. The DOS are calculated without including the SOC effect.

that this interface forms a p-type Ohmic contact. In contrast, for Te-terminated Ni/Bi$_2$Te$_3$ and Co/Bi$_2$Te$_3$ interfaces, the calculated $\Phi_p$ are 0.2 and 0.28 eV. This means that in both cases the Fermi lies above the Bi$_2$Te$_3$ CB edge and gives an n-type Ohmic contact if we use the experimental band gap of 0.16 eV. The calculated band offsets of these interfaces are consistent with the experimental observation. Thus, the band offset strongly depends on the interfacial bonding. Similarly, we calculated $\Phi_p$ for NiTe/Bi$_2$Te$_3$ and CoTe$_2$/Bi$_2$Te$_3$ interfaces and found that they all give an Ohmic contact, as summarized in table 1.

The formation of different types of Ohmic contact with respect to the termination of the interfaces can be explained in terms of local bonding. The formation of the metal/semiconductor interface causes charge transfer from the metal to the semiconductor, due to their different
Figure 6. Projected DOS of (a) Bi-terminated and (b) Te-terminated Ni/Bi$_2$Te$_3$ interfaces, (c) Bi-terminated and (d) Te-terminated Co/Bi$_2$Te$_3$ interfaces, (e) Ni–Bi NiTe/Bi$_2$Te$_3$ and (f) Co–Bi CoTe$_2$/Bi$_2$Te$_3$ interfaces. The DOS are calculated with the SOC effect.

electronegativities (ENs). Despite the small differences of EN values (Pauling criterion) of the elements in our system (Ni: 1.9, Co: 1.88, Bi: 2.02, Te: 2.1), the formation of dipoles at different interface configurations makes the Fermi level easily sweep across the small band gap of Bi$_2$Te$_3$. The larger $\Phi_p$ of Te-terminated Ni(Co)/Bi$_2$Te$_3$ interfaces as compared with that of Bi-terminated interfaces is similar to what was found previously for metal/III–V (or II–VI) semiconductor interfaces [25]. It has been reported that the interface terminated by the anion of semiconductor has larger $\Phi_p$ than that terminated by the cation, due to the dipole formation between the charge at the semiconductor surface and its image charge at the metal.
Moreover, it is interesting that NiTe and CoTe$_2$ also form Ohmic contacts on Bi$_2$Te$_3$. This indicates that Co and Ni are suitable contact materials. Co is a better choice because of its low diffusivity. However, it should be noted that although our results are in agreement with the experimental data, the effects of interface defects (e.g. dopant, vacancy, etc) and interfacial layers (e.g. oxidation) should not be neglected. In particular, for addressing the contact resistance issues, these extrinsic effects would change the interface chemistry and hence modify the entire electronic structure of the interface. We have studied the impact of oxygen at these interfaces, which will be published elsewhere, and found that oxygen indeed affects the electronic structure of the interfaces. Therefore, to achieve low contact resistance, we should consider the overall effect by including all these aspects.

4. Conclusion

In summary, first-principles calculations of band offsets and stability of Ni/Bi$_2$Te$_3$, NiTe/Bi$_2$Te$_3$, Co/Bi$_2$Te$_3$ and CoTe$_2$/Bi$_2$Te$_3$ interfaces are presented. The formation energies of Co/Bi$_2$Te$_3$ interfaces are much lower than Ni/Bi$_2$Te$_3$ interfaces, making the Ni/Bi$_2$Te$_3$ interface more prone to reaction as temperature is increased. Moreover, NiTe is found to be more stable on Bi$_2$Te$_3$ than Ni, while the formation energy for CoTe$_2$ on Bi$_2$Te$_3$ is comparable to that of Co. Our results are in agreement with the experimental data. All the interfaces give Ohmic contacts, indicating Ni and Co are suitable contact materials for Bi$_2$Te$_3$.

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