Thermodynamic Stability of Ni/Sb$_2$Te$_3$ Interface by First-Principles Calculations

H. H. Hsu[1], C. H. Cheng[2], C. H. Huang[3], S. H. Chiou[3], Y. L. Lin[1], M. C. Lin[1], C. C. Wu[1] and Y. C. Lee[1]

[1]Green Energy and Environment Research Lab., Industrial Technology Research Institute, Hsinchu, Taiwan, R.O.C.

[2]Department of Mechatronic Technology, National Taiwan Normal University, Taipei, Taiwan, R.O.C

[3]Material and Chemical Research Lab., Industrial Technology Research Institute, Hsinchu, Taiwan, R.O.C.

E-mail address: HHHsu@itri.org.tw

Solid-state thermoelectric devices have been attracting considerable attention for the applications of cooler and power generation. The high-performance crystalline Sb$_2$Te$_3$ and its solid solution with Bi substitution, (Sb$_x$Bi$_{1-x}$)$_2$Te$_3$, to enhance thermoelectric properties of ZT ($=S^2T\sigma/\kappa$) has been proposed and demonstrated [1,2], where S is Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity. A low-cost Ni has been utilized as a diffusion barrier between Cu and thermoelectric elements. However, a pending issue related to poor thermo-stability on thermoelectric material still remains unsolved. To address this issue, we made a systematic comparison of calculating interface formation energy for Ni/Sb$_2$Te$_3$ samples with different terminated surfaces to discover the energetic favorable interface configurations. To clarify the interface stability at Ni/Sb$_2$Te$_3$ interfaces, the Sb- and Te-terminated Sb$_2$Te$_3$ in direct contact with Ni barrier was computed by relaxing 2x2x1 supercell with constrained Sb$_2$Te$_3$, where unit cell was defined to contain six Sb and nine Te atoms as shown in Figure 1. The interfaces were modeled by a superlattice including one interface and a 17 Å vacuum layer on top. Subsequently, the first principles calculations using the total energy plane-wave basis code VASP [3] were performed to investigate the impact of various configurations of Sb and Te termination.

In equation 1, the interface formation energies as a function of tellurium chemical potentials can be defined as [4]:

$$E_{Fromation}^{Ni/Sb_2Te_3} = E_{Total}^{Ni/Sb_2Te_3} - \alpha E_{Sb_2Te_3} - \beta E_{Ni} - \gamma \mu_{Te} \quad (1)$$

where E_{Total}^{Ni/Sb_2Te_3} is the total energy of the given supercell. $E_{Sb_2Te_3}$ and E_{Ni} are the total energies per formula unit in Sb$_2$Te$_3$ and Ni, respectively. α and β are the corresponding number of Sb$_2$Te$_3$ and Ni bulk units in the slab, respectively. γ is the number of excess or deficient Te atoms. μ_{Te} is the tellurium chemical potential, which is the only one independent parameter determinate by the film deposition conditions. μ_{Te} maximum equals to μ_{Te}^{Bulk}, suggesting Te-rich condition. μ_{Te} minimum can be described as: $\mu_{Te} = \mu_{Te}^{Bulk} + \frac{1}{3}\Delta H$, where ΔH is the formation enthalpy of bulk Sb$_2$Te$_3$ close to -0.48 eV [5], suggesting Sb-rich condition. As shown in Figure 2, the interface formation energy of Sb-terminated Ni/Sb$_2$Te$_3$ structure apparently decays with increasing μ_{Te}, while Te-terminated interface maintains a constant value, implying that the Sb-terminated surface with smaller formation energy provides a more stable configuration for Ni barrier contact interface, compared to Te-terminated one. The

first principles results are also supported by Ni/Bi$_2$Te$_3$ case [6]. Thus, our finding clearly explains the preferred formation of NiTe-based compounds near contact interface with Te termination, which can lead to undesired interface diffusion and degraded bulk ZT value due to nonstoichiometric Sb$_2$Te$_3$, even at a low soldering temperature.

References
[1] G. Kavei and M. A. Karami, *Bull. Mater. Sci.*, **29**, 659, (2009).
[2] C. Wood, Rep. Prog. Phys. 51, 459 (1988)
[3] G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, **6**, 15 (1996) ; G. Kresse and J.Furthmuller, Phys. Rev. B, 54, 11169 (1996).
[4] V. Fiorentini and G. Gulleri, *Phys. Rev. Lett.* **62**, 266101(2002).
[5] V. Piacente *et al., Journal of Alloys and Compounds,* **178**, 101 (1992).
[6] R. P. Gupta *et al., Electrochemical and Solid-State Letters*, **12**, H395 (2009).

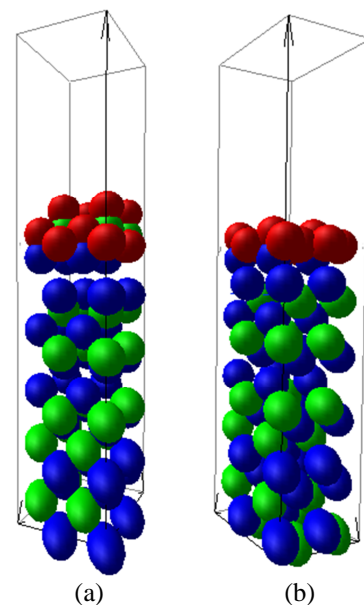Fig. 1. The relaxed atomic structure of Sb$_2$Te$_3$ in contact with Ni barrier with (a) Sb and (b)Te-terminated surface. (red: Ni atom, green: Sb atom, blue: Te atom)
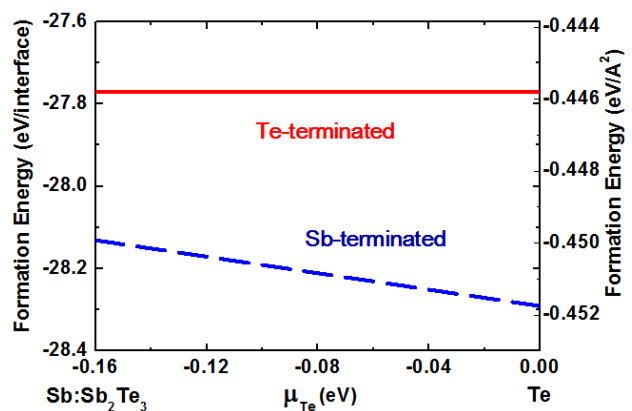

Fig. 2. Interface formation energies of Sb and Te-terminated Ni/Sb$_2$Te$_3$ versus Te chemical potential.