Bottom-Up Metal/Oxide/Bi₂Te₃ Heterostructures for Enhanced Thermoelectric Properties [†]

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Abstract: In this paper, metals' (Cu, Ag, Au)/Al₂O₃/Bi₂Te₃ heterostructures have been fabricated to synergistically optimize their carrier concentration and mobility, thereby enhancing their thermoelectric power factor. Metal can be alloyed with Bi₂Te₃ to reduce the electron concentration. The introduction of the oxide layer further reduces the electron concentration and leads to an increase in mobility. By adjusting the metal and oxide layer, it is possible to realize the simultaneous optimization of electric conductivity and the Seebeck coefficient. This work will enable the optimal and novel design of heterostructures for thermoelectric materials with further improved performance.

Keywords: heterostructure; thermoelectric; metal particle; interface

1. Introduction

Thermoelectric technology can convert heat to electricity freely. The thermoelectric efficiency is normally expressed by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. One strategy to improve the thermoelectric performance is fabricating nanostructures such as pores or nanograins, which could strongly scatter phonons and thereby reduce the lattice thermal conductivity. However, little room remains for further reducing κ . On the one hand, the contribution of electrons to thermal conductivity is unavoidable due to the Wiedemann–Franz law. On the other hand, the lattice thermal conductivity cannot be lower than the amorphous state. For the Bi₂Te₃ system, the lattice thermal conductivity has approached values as low as $\sim 0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is the limit value predicted by the Cahill model.[1] Further improvements in the ZT could rely on decoupling S and σ to improve the power factor ($\text{PF} = S^2\sigma$). In this paper, metals' (Cu, Ag, Au) and Al₂O₃ interfaces were introduced in Bi₂Te₃ film to explore methods to improve the power factor.

2. Materials and Methods

Metals' (Cu, Ag, Au) with a thickness of 6–7 nm were pre-deposited on a SiO₂/Si substrate by an e-beam evaporation system. Using alloy targets, the Al₂O₃ layer, with a thickness of $\sim 3 \text{ nm}$, is first selectively sputtered on the metal, followed by a Bi₂Te₃ film with a thickness of 300 nm. The Al₂O₃ deposited at 100 W and Bi₂Te₃ deposited at 50 W were both in a radio frequency (RF) mode. The purity of all source materials is 99.99%. The sample preparation is shown in Figure 1a.

3. Results and Discussions

The pre-deposited metal presents as discontinuous particles, as shown in Figure 1b–d. Regardless of whether metal/oxide is deposited, there is no obvious difference in the surface morphology of the Bi₂Te₃ film, the surface of which is selected as shown in the Figure 1e. The XRD pattern shown in Figure 1f shows that the obtained Bi₂Te₃ is with good crystallinity. Thermoelectric properties of Bi₂Te₃-based heterostructures are shown in Figure 1g–k. The metal will alloy with Bi₂Te₃ (such as Ag₂Te or Cu₂Te, et al.), thereby reducing the electron carrier concentration [2], which is confirmed in Figure 1k. The doping and alloying effects of metals with different activity are different. The introduction of the oxide layer prevents this alloying process, and scatters part of the carrier, as shown in Figure 1l. Some carriers may tunnel through the thin oxide layer from the metal into Bi₂Te₃. On the other hand, due to the existence of pores in the local region of the thin oxide layer, it is inevitable that some metal atoms could pass through the oxide layer and be doped into the Bi₂Te₃. The combined effect of the above factors can optimize the carrier concentration and mobility, thereby enhancing the power factor ($S^2\sigma$) according to Mott's expression:

$$S = \left(\pi^2 k_B^2 T / 3q \right) \left\{ dn(E) / ndE + d\mu(E) / \mu dE \right\}_{E=E_F} \quad (1)$$

where $n(E)$ and $\mu(E)$ are the carrier concentration and carrier mobility depending on energy, respectively. E_F is the Fermi energy. k_B is the Boltzmann constant, and q is electron charge.

Figure 1. Preparation, characterization and thermoelectric performance of Bi₂Te₃-based films. (a) Preparation of Bi₂Te₃-based films in the order of depositing metal, Al₂O₃ and Bi₂Te₃; (b), (c) and (d) are the top view of Cu, Ag and Au, respectively; (e) the surface morphology of Bi₂Te₃; (f) the XRD pattern of Bi₂Te₃ film; (g) electrical conductivity; (h) Seebeck coefficient; (i) power factor; (j) carrier mobility; (k) carrier concentration; (l) crossing and scattering of electrons at the interface. BT represents Bi₂Te₃.

4. Conclusions

In summary, metals' (Cu, Ag, Au)/Al₂O₃/Bi₂Te₃ heterostructures have been fabricated to improve their thermoelectric properties. The introduction of metals and oxide interface synergistically adjust their carrier concentration and mobility, thereby optimizing their thermoelectric power factor. The power factor of the Cu/Al₂O₃/Bi₂Te₃ heterostructure film is 6.5 $\mu\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$, which is 1.75 times that of a single Bi₂Te₃ film.

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