

Plating of Bi(Sb)Te Alloys for Thermoelectric Applications

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Introduction

Thermoelectric cooling is an attractive solid-state electronic refrigeration solution that offers a compact, lightweight, reliable, and environmentally friendly alternative to vapor compression refrigerators. The cooling flux per unit area $> 100 \text{ W/cm}^2$ can be attained by scaling the length of the thermoelements and adopting thin-film fabrication techniques. The efficiency of thermoelectric coolers can be increased by enhancing the thermoelectric figure-of-merit

$$ZT = S^2 \sigma T / \kappa$$

that depends on the Seebeck coefficient S , the electrical conductivity σ , the thermal conductivity κ , and the absolute temperature T . A variety of promising approaches such as transport and confinement in quantum dots, nanowires, superlattices, and device structures using sharp point contacts at the cold end have been proposed to increase ZT . Our early experiments on the latter "cold point cooler" prototypes indicate doubling of ZT values to the range of 1.4-1.7 (1), and further advances in sharpening the points and applying thermoelectric overcoats on tips could yield $ZT > 3$, i.e. performances better than the vapor compression refrigerators. Electrodeposition has played a significant role in the development of these thin film thermoelectric coolers and the overcoats on cold point structures.

Plating of thermoelectric alloys of the $\text{Bi}(\text{Sb})_x\text{Te}_{1-x}$ family poses several challenges:

- Stiff structures such as the "cold points" mentioned above are best made of high conductivity refractory metals such as Pt, Mo, W. Plating of continuous, uniform films on these substrates is difficult, in the case of Pt because of hydrogen evolution, in the case of Mo and W probably because of their protective oxide layer.
- When plating very thin films (10-20 nm), good coverage has to be secured, requiring extensive nucleation of the thermoelectric semiconductor on a substrate of different structure.
- Good control of the composition is essential, since the figure-of-merit Z depends on it.

- The stability range of solutions is limited by hydrolysis and precipitation tendencies.

Experimental

In the present work, previous accounts of plating of Bi(Sb)Te alloys (2, 3) were used for guidance. Plating was performed in an RDE setup, using a Pt mesh anode. The plating solutions were generally 0.5-1.0 M in nitric acid, often (especially where Sb was included) 0.13-0.20 M in tartaric acid, 8 mM in Bi nitrate, usually 3-12 mM in Te^{4+} . It was shown that methanesulfonic acid can replace nitric acid. It was confirmed that, for a wide range of current densities and Bi/Te ratios in solution, the Bi/Te ratio in the deposit remains relatively close to 2/3. Interestingly, Sb^{3+} strongly affects the Bi/Te ratio in the deposit even when little Sb is deposited.

While deposition of $\text{Bi}_x\text{Te}_{1-x}$ on Ni and Au was straightforward, deposition on other substrates required various additives. For Pt, addition of a surfactant (FC-95) helped ensure complete coverage. Plating on Mo and W required addition of HF (0.05, respectively 0.2 M). Deposition of Sb-containing films on Pt required the interposition of a thin sputtered Bi layer.

The plating of alternating thin films of Bi_2Te_3 and Sb_2Te_3 (5 pairs) was demonstrated, by alternating plating from different solutions. Such stacked films could be used after high-temperature annealing to generate a thermoelectric element of well-defined properties. In another variation, which led to an improved Seebeck coefficient, thin film plating and thermal annealing in nitrogen were alternated. Annealing at 300°C causes substantial reaction between $\text{Bi}_x\text{Te}_{1-x}$ and Pt substrates, as opposed to no reactivity toward Mo and W. Plating of $\text{Bi}_x\text{Te}_{1-x}$ on Pt/Ti and Pt/Cu/Ti "cold points" was demonstrated. As expected, the film was richer in Te (the nobler component) near the tip than elsewhere.

References

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