Fabrication and Characterization of Contacts for Chalcopyrite-Based Thermoelectric Module

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Abstract:

Approximately 66% of the energy consumed in applications such as automobiles, factories, incinerators, powers plants and other machinery is lost to waste heat, a majority of which is under 150°C [1]. The ability to efficiently harness this lost energy for other applications would revolutionize energy consumption in society. Therefore efforts in the thermoelectric industry focus on the development of ZT-enhanced thermoelectric materials such as n-type chalcopyrite for low temperature ranges [2]. In a recent collaboration the Thermal Energy Harvesting Group observed efficiency losses in a fabricated thermoelectric module due to poor electrical contact at the junction between the electrode and the thermoelectric material. The goal of this study is to survey potential contacts metals for n-type chalcopyrite and develop a high throughput one-step spark plasma sintering fabrication method to ease device fabrication. It was observed that the amount of diffusion of the metal into the thermoelectric material has a direct relationship to the bond adhesion and an inverted relationship to the maintenance of thermoelectric properties. Large diffusive regions hinder thermoelectric performance while minimal diffusion limits bond strength and thus the lifetime of the device.

Summary of Research:

Thermoelectric Leg Fabrication. The Zn-doped chalcopyrite powder is solidified by spark plasma sintering (SPS). It is placed in a graphite die and put under a pressure of 40 MPa in an argon gas atmosphere. A current is run through the chamber of the graphite die while undergoing the temperature schedule (5 min rising to 500°C, 5 min holding at 500°C, 10 min cooling to 200°C) as seen in Figure 1. The following thermoelectric leg structures were fabricated with this method: powder/chalcopyrite powder, powder/foil/chalcopyrite powder, foil/chalcopyrite powder [2-4].

Thermoelectric Leg Characterization. After solidification by SPS, the samples were cut by a dicing saw to have a rectangular cross-section with a width and length on the order of ~ 2-4 mm and polished. The thermoelectric properties of the samples were then measured with ZEM-2 Analysis. In addition, XRD was utilized to analyzed composition of thermoelectric material post-SPS [2].

Results and Conclusions:

High Diffusion/Reaction Rate Limits Fabrication. After benchmarking the fabrication process and thermoelectric properties of standard n-type chalcopyrite, Cu powder was surveyed as a potential contact for the thermoelectric material due to its abundancy in lab. After the sintering process was run, the thermoelectric region was observed to be a gray region contradicting the green-gold color that was expected to be produced indicating the presences of a high amount of diffusion during the fabrication process. It was then characterized by ZEM analysis and it was found that the power factor was approximately zero in comparison to the magnitude of the power factor of the standard n-type chalcopyrite. The thermoelectric properties can be viewed in Figures 2 and 3. Au (5 µm) and Ni (125 µm) foil were then employed to limit the diffusion of the Cu into the thermoelectric material [5]. In both cases the produced color of the thermoelectric region indicated a reduction in Cu diffusion however

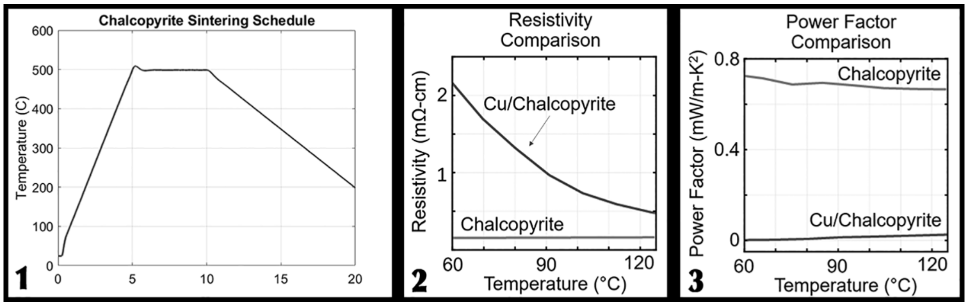

Figure 1, left: *Graph of temperature schedule for spark plasma sintering process.* ***Figure 2, middle:*** *Graph of resistivity of Cu/Chalcopyrite stack as compared with n-type chalcopyrite.* ***Figure 3, right:*** *Graph of power factor of Cu/Chalcopyrite and n-type chalcopyrite.*

there we clear Au and Ni diffusion regions indicated by a different colored layer. While the diffusion in the Ni sample allowed for bond adhesion, the Ni diffusion affects the produced thermoelectric properties.

Limited Diffusion Weakens Foil Adhesion. In response to observing high amounts of diffusion affect the thermoelectric properties, metals that were unlikely to diffuse at high rates in chalcopyrite based on Hume-Rothery rules were tested as potential contacts: 250 µm Ti foil/chalcopyrite powder, Mo powder/50 µm Ta foil/chalcopyrite powder. In both cases total delamination occurred due to the limited solid-state diffusion during the sintering process [3].

Conservation of Chalcopyrite vs. Adhesion. XRD patterns were measured for the Cu powder/chalcopyrite powder, Cu powder/125 µm Ni foil/chalcopyrite powder, 250 µm Ti foil/chalcopyrite powder. As seen in Figure 4, the consumption of the chalcopyrite produces a greater contact adhesion. However, if the chalcopyrite is consumed the thermoelectric properties will be diminished, therefore there must be a balance between contact adhesion and maintenance of thermoelectric properties.

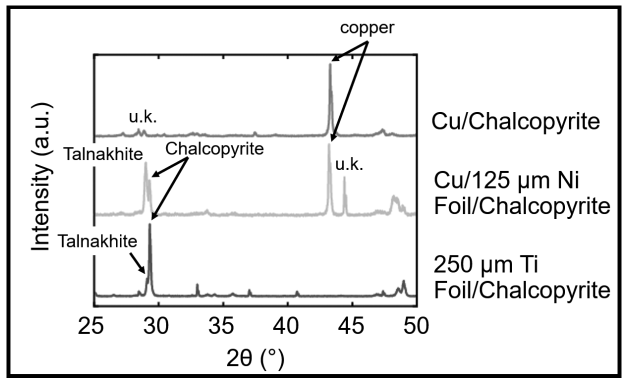

Figure 4: XRD patterns of Cu powder/chalcopyrite powder, Cu powder/125 µm Ni foil/chalcopyrite powder, 250 µm Ti foil/chalcopyrite powder demonstrating relation of adhesion to consumption of chalcopyrite.

Future Work:

Based on the specifications outlined in this work, further investigation into what type of contact material and form will be necessary. After the fabrication and evaluation of a successful contact material, a thermoelectric module will be fabricated and its efficiency lifetime will be characterized.

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