FABRICATION OF COPPER/COPPER-NICKEL THIN-FILM THERMOELECTRIC GENERATORS WITH ENERGY STORAGE DEVICES

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Abstract. We demonstrated the fabrication of Cu/Cu-Ni thin-film thermoelectric generators for energy harvest. The thin-film generator consisted of 50 pairs of Cu/Cu-Ni thermocouples. The widths of Cu and Cu-Ni thermoelectric elements were 75 μm and 225 μm, respectively. The length of the both elements was 5 mm. Cu and Cu-Ni thin-films were deposited on polyimide substrates with low thermal conductivity using radio-frequency magnetron sputtering method and formed by lift-off techniques. Then, the thin-film generators were coated with polyimide thin films. The generation properties of the fabricated device, which consisted of serially-connected 15 thin-film generators, were evaluated. When the hot side of the device was heated at 203°C using a hot plate as a thermal source, the temperature difference between the hot and cold sides was approximately 70°C. The open-circuit voltage and maximum power were 2.18 V and 21 μW, respectively. A commercially-available light emission diode was successfully operated by connecting the device to a capacitor for energy storage.

1. Introduction

Energy harvesting devices using light, vibration and thermal energy have attracted attention in Internet of Things (IoT) society because these devices can supply electric energy to stand-alone sensors in the networks [1-2]. Thermoelectric microgenerators create power in micro watts by converting temperature gradient into electric energy using the Seebeck effect [3], and can utilize relatively low temperature (less than 300°C) waste heat which has not been widely used so far. We have fabricated Bi-Te thin-film thermoelectric generators that exhibit excellent figure of merit [4]. However, there are disadvantages that the materials consist of scarce metals, and the toxicity and difficulty of microfabrication due to brittleness. In this study, we demonstrated the fabrication of thin-film thermoelectric generators using Cu-Ni thermoelectric alloys that are well-known as thermoelectric materials and exhibit excellent microfabrication properties. Then, the generation properties of the fabricated device that consisted of serially-connected 15 thin film generators were evaluated. The figures of merit of these materials are generally lower due to their high thermal conductivities, resulting that it is difficult to generate temperature differences in the bulk Cu-Ni alloys. Our proposed device enabled to generate a large temperature difference between the hot and cold sides of the pn junctions by using Cu-Ni thermoelectric elements that are sufficiently thinner than the substrates with low thermal conductivity.
2. Experimental methods

2.1. Design of thin-film thermoelectric generator
A design of thin-film thermoelectric generator is shown in figure 1. The generator consisted of 50 pairs of thermocouples, Cu (p-type) and Cu-Ni (n-type) thin-film thermoelectric elements. The widths of the Cu and Cu-Ni elements were 75 μm and 225 μm, respectively. The thickness and length of the both elements were 200 nm and 5 mm, respectively. The elements were fabricated on polyimide substrates with low thermal conductivity (0.29 W/mK), compared to that of Cu (386 W/mK) and Cu-Ni (23 W/mK). The thickness of polyimide substrates was 50 μm.

![Figure 1. Schematic of thin-film thermoelectric generator.](image1.png)

2.2. Fabrication process of thin-film thermoelectric generator
Figure 2 shows the fabrication process of the thin-film thermoelectric generator. Cu and Cu-Ni thin films were deposited by radio-frequency (RF) magnetron sputtering method and were formed by lift-off techniques. Cu and Cu_{60}Ni_{40} alloy targets were used for the film depositions. Then, polyimide thin films were coated on the thin-film generators using a photosensitive polyimide (Toray, Photoneee, PW-1500). The RF power and Ar process gas pressure for Cu and Cu-Ni thin-film depositions were 30 W and 1.0 Pa, and 40 W and 0.5 Pa, respectively. The base pressure and deposition time was 3.0×10^{-3} Pa or less and 10 min, respectively. The photosensitive polyimide was baked at 140°C, 240°C, and 340°C for 5 min each. Electrical resistivities of the both films were measured by a four-probe method. Cu-Ni thin-film was examined using X-ray diffraction (XRD) analysis (Rigaku, RINT RAPID-S).

![Figure 2. Schematic of fabrication process of the thin-film thermoelectric generator.](image2.png)

2.3. Evaluation method of thermoelectric device
The generation properties of the fabricated device (750 pairs), which consisted of serially-connected 15 thin-film thermoelectric generators, were evaluated. Generation voltage and output power were evaluated by heating the hot side of the device at approximately 200°C using a hot plate as a thermal source. In addition, the device was connected to a capacitor (220 μF) for energy storage, following that a commercially-available light emission diode (LED) was operated by using the energy.

3. Results and discussion

3.1. Fabrication of thin-film thermoelectric generators
The electrical resistivities of Cu and Cu-Ni thin-film were 7.7 μΩ cm and 67 μΩ cm, respectively, which were almost the same as the electrical resistivities of the bulk materials. Figure 3 shows XRD spectrum of Cu-Ni thin film deposited on polyimide substrate. The diffraction peaks corresponding to Cu-Ni were observed although those of the oxidation of the thin-film were not observed. This result indicates that high purity Cu-Ni thin films were deposited by the RF sputtering method.
The thin-film thermoelectric generator and the device containing the 15 thin-film generators are shown in figures 4 and figure 5, respectively. The thermoelectric thin-film elements were successfully formed on the polyimide substrates without large deformation of the substrate. The internal resistance of the thin-film generator was 3.7 kΩ and the their serially-connected device was 56 kΩ. These values indicate that the contact resistance of each thin-film thermoelectric generator was negligibly small. The size of the thermoelectric device shown in figure 5 was 10×25×3 mm³.

3.2. Evaluation of thermoelectric device

Figure 6 shows generation properties of the device. When the hot side of the device was heated at 203°C, the temperature difference between the hot and cold sides of pn junctions was approximately 70°C. The open-circuit voltage and maximum power were 2.18 V and 21 μW, respectively.

The device was connected to the capacitor and LED. Figures 7 show the circuit diagram and photograph of actual circuit. The charge characteristic of the capacitor which was connected to the device is shown.
in figure 8(a). The power of 4.6×10^2 μJ was charged into the capacitor for 60 s. Furthermore, the LED was successfully operated using the charging energy as shown in figure 8(b). The thermoelectric generators with storage devices is expected to be used to supply electric energy to stand-alone devices.

![Circuit diagram and photograph of the fabricated device with energy storage circuit.](image)

Figure 7. (a) Circuit diagram and (b) photograph of the fabricated device with energy storage circuit.

![Graph showing charge characteristics and LED operation.](image)

Figure 8. (a) Charge characteristics using a capacitor (220 μF) and (b) LED operation by the serially-connected device (750 pairs).

4. Conclusions
Cu/Cu-Ni thin-film thermoelectric generators were fabricated by sputtering method and lift-off techniques. The generation properties of the fabricated device (750 pairs), that consisted of 15 thin-film generators, were evaluated. When the temperature difference between the hot and cold sides was created as approximately 70°C using the heat source at 203°C, the open-circuit voltage and maximum power were 2.18 V and 21 μW, respectively. The LED were successfully operated by connecting the serially-connected device to the capacitor for energy storage.

5. References
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