REGULAR PAPERS

Fabrication of thin-film thermoelectric generators with ball lenses for conversion of near-infrared solar light

To cite this article: Yoshitaka Ito et al 2017 Jpn. J. Appl. Phys. 56 06GN06

View the article online for updates and enhancements.

Related content

- Fabrication of CuO-based antireflection structures using self-arranged submicron SiO$_2$ spheres for thermoelectric solar generation
  Tasuku Kondo, Mizue Mizoshiri, Masashi Mikami et al.

- Thermal–Photovoltaic Hybrid Solar Generator Using Thin-Film Thermoelectric Modules
  Mizue Mizoshiri, Masashi Mikami and Kimihiro Ozaki

- The effect of Cr buffer layer thickness on voltage generation of thin-film thermoelectric modules
  Mizue Mizoshiri, Masashi Mikami and Kimihiro Ozaki
Fabrication of thin-film thermoelectric generators with ball lenses for conversion of near-infrared solar light

Yoshitaka Ito1, Mizue Mizoshiri1*, Masashi Mikami2, Tasuku Kondo1, Junpei Sakurai1, and Seiichi Hata1

1Department of Micro-Nano Systems Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
2National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan

*E-mail: mizoshiri@mech.nagoya-u.ac.jp

Received November 30, 2016; revised January 19, 2017; accepted February 7, 2017; published online May 12, 2017

We designed and fabricated thin-film thermoelectric generators (TEGs) with ball lenses, which separated visible light and near-infrared (NIR) solar light using a chromatic aberration. The transmitted visible light was used as daylight and the NIR light was used for thermoelectric generation. Solar light was estimated to be separated into the visible light and NIR light by a ray tracing method. 92.7% of the visible light was used as daylight and 9.9% of the NIR light was used for thermoelectric generation. Then, the temperature difference of the pn junctions of the TEG surface was 0.71 K, determined by heat conduction analysis using a finite element method. The thin-film TEGs were fabricated using lithography and deposition processes. When the solar light (A.M. 1.5) was irradiated to the TEGs, the open-circuit voltage and maximum power were 4.5 V/m² and 51 µW/m², respectively. These TEGs are expected to be used as an energy supply for Internet of Things sensors.

© 2017 The Japan Society of Applied Physics

1. Introduction

Recently, energy-harvesting devices have attracted attention in the Internet of Things (IoT) and Trillion Sensors Universe to supply electric power to the IoT sensors.1,2) These devices, which generate several hundreds of microwatts and are used with storage systems, convert waste energy in the environment into electric energy. Ambient energy sources such as vibration, light, and heat are used for energy harvesting. For example, vibration energy is converted to electric energy by piezoelectric devices.3–5) Light energy such as solar and artificial light is converted to electric energy using photovoltaic cells.6–12) Thermal energy creates a temperature gradient, which is converted to electric energy using thermoelectric generators (TEGs).13–23)

Solar light is a promising renewable energy, which has a wide spectrum from ultraviolet light to near-infrared (NIR) light. Visible light, which is approximately 53% of solar light, is used as daylight in our lives and is converted to electric energy using photovoltaic generation systems. However, the NIR light, which is approximately 42% of solar light, cannot be efficiently converted into electric energy using the photovoltaic effect. Moreover, the conversion efficiency of c-Si photovoltaic cells is decreased by increasing the cell temperature by NIR light irradiation.15,16)

To use the NIR light effectively, thermal-photovoltaic hybrid generators have been utilized. The hybrid generators, which are composed of photovoltaic cells and TEGs, convert the visible light and NIR light into electric energy using the photovoltaic and thermoelectric (TE) effects, respectively.21,26–29) It is important for TEGs to create a large temperature gradient between the hot and cold sides of pn junctions because the generation voltage linearly increases with the temperature gradient and the generated power is increased with the square of the temperature gradient.

Thin-film TEGs can be classified into two types: a vertical type and a planar type. In the vertical TEGs, the temperature gradient is created in the thickness direction of the thin-film TE elements. On the other hand, the planar TEGs convert the temperature gradient in the thin-film TE elements to electric energy. In thin-film TEGs, it is difficult to improve the generation performance of the vertical type because a large temperature gradient cannot be generated in the thin films in the thickness direction.13–17) In the planar TEGs, the temperature gradient can be controlled by changing the length of the TE elements.18–23) To date, we have also fabricated thermal-photovoltaic hybrid generators, which are composed of thin-film TEGs and commercially available photovoltaic cells, hot mirrors, and focal lenses. The thin-film TEGs converted the NIR light, which was separated from full solar light. The NIR light was focused onto the hot sides of thin-film TEGs using the focal lens. However, the hybrid generators have a relatively large volume to be set on the IoT sensors and ambient goods such as windows, because they are composed of bulk mirrors and lenses. If small and visibly transparent TEGs are developed, the NIR light can be used as an energy source effectively and the visible light can be used as daylight when the TEGs are set on transparent materials.

In this study, we proposed visibly transparent thin-film TEGs with small ball lenses that can be used by setting on glass windows. The thin-film TEGs with ball lenses were designed to transmit the visible light and convert the NIR light to electric energy using a chromatic aberration induced by the small ball lenses. With the calculation using a ray tracing method and a finite element method (FEM), the TEGs with pinholes and the ball lenses, which separated the visible light and NIR light using the chromatic aberration, were designed. The ball lenses focused the NIR light onto the hot sides of the TEGs and transmitted the visible light to the glass substrate. Then, we demonstrated the fabrication of the TEGs with ball lenses and evaluated the thermoelectric generation properties.

2. Design of thermoelectric generator

2.1 Design concept

Figure 1 shows a schematic illustration of the thin-film TEGs with small ball lenses. The TEGs were serially connected as shown in Fig. 1(a), to generate a large voltage. The number of TEGs was 111. The small ball lenses were set at the center of a pinhole. When the ball lenses were used to focus full solar light, the light was separated into the visible light...
and NIR light by using the chromatic aberration of the wavelength dependence. The visible light was focused onto the center of the pair of pn junctions, which passed through the transparent glass substrate. The visible light was used as daylight. In contrast, the NIR light was defocused and irradiated onto the hot side of the TE elements, as shown in Fig. 1(b). The temperature gradient between the hot side of the TE elements and the cold side of the circumference of the TE elements generated the TE voltage.

### 2.2 Simulation method

A theoretical analysis of the focusing properties of solar light using the small ball lenses was performed using a ray tracing method (OSLO EDU), which was used to geometrically calculate the path of the light propagation depending on the wavelength. The simulation models and parameters are shown in Fig. 2(a) and Table I, respectively. The radius of a pinhole was determined as the $\frac{1}{e^2}$ radius of the focal spot at the maximum visible wavelength (assumed as 800 nm) because the focal spot increased with increasing wavelength. The pinhole radius was 26 μm by considering the calculation result.

The energy that passed through the pinhole at a wavelength in the solar light $\lambda$ was defined as $E_{\lambda}(\lambda)$ and the solar energy at the wavelength $\lambda$ was defined as $E(\lambda)$. Then, the transmittance $t(\lambda)$ through the pinhole at the wavelength $\lambda$ was described as

$$ t(\lambda) = \frac{E_{\lambda}(\lambda)}{E(\lambda)} \quad (1) $$

The transmittance of the visible solar light at wavelength from 280 to 800 nm, $T_{\text{vis}}$, is described as

$$ T_{\text{vis}} = \frac{\int_{\lambda=280nm}^{\lambda=800nm} t(\lambda) \cdot \frac{E_{\lambda}(\lambda)}{E(\lambda)} \, d\lambda}{\int_{\lambda=280nm}^{\lambda=800nm} \frac{E(\lambda)}{E(\lambda)} \, d\lambda} \quad (2) $$

If all the visible solar light at wavelengths from 280 to 800 nm was transmitted inside the pinhole, $T_{\text{vis}}$ was 100%. The irradiation rate of the NIR light at wavelengths from 800 to 4000 nm, $U_{\text{NIR}}$, is described as

$$ U_{\text{NIR}} = \int_{\lambda=800nm}^{\lambda=4000nm} 1 - t(\lambda) \cdot \frac{E(\lambda)}{E(\lambda)} \, d\lambda \quad (3) $$

The temperature gradient of the thin-film TEGs was calculated by FEM heat conduction analysis (COMSOL Multiphysics). The heat flux by the NIR light, which exhibited different focal spot radii depending on the wavelength, was assumed by considering each focal spot diameter and solar light energy at the wavelength. The focal spot radius was determined as the $\frac{1}{e^2}$ radius of the focal spot at each wavelength. Both the visible light (280–800 nm) and NIR light (800–4000 nm), which were irradiated inside the pinhole, were transmitted through the glass substrate. The transparence of both types of light was experimentally determined to be 90%. Therefore, 10% of the energy irradiated inside the pinhole was assumed to be absorbed by the glass substrate. In contrast, 100% of the visible light and NIR light, which were irradiated outside the pinhole, were assumed to be absorbed by the electrode and TE elements and converted into thermal energy without energy.
loss. The temperature distribution at the steady state was calculated. Commercially available small ball lenses (sapphire, Edmund Optics) were used in the TEGs. The materials of the TEGs were as follows. Bi$_0.5$Sb$_1.5$Te$_3$ and Bi$_2$Te$_2.7$Se$_{0.3}$ were used as p- and n-type thin-film TE elements, respectively. Cu thin films were used as the electrodes. It is expected that the temperature difference underlying the Cu electrodes cannot contribute to the TE generation because the TE elements form a closed circuit with Cu electrodes. Therefore, the width of Cu electrodes was determined to be 50 µm, which was small and exhibited a small resistance. SiO$_2$ thin films were overcoated onto the TE elements and the electrodes to prevent oxidization. Table II shows the material properties. Figure 2(b) exhibits a two-dimensional model of the cross section of the TEGs for the heat conduction analysis. The boundary conditions on the center and circumference lines were determined as the heat insurance, because the TEGs were periodically formed, as shown in Fig. 1(a). The other boundaries were determined to be natural conversion. The heat transfer coefficient was determined to be 5 W/m$^2$K. The minimum and maximum mesh sizes in FEM were 20 nm and 10 µm, respectively.

### 2.3 Simulation result of TEGs

Figure 3(a) shows two of all the calculated intensity distributions of the focused solar light at 800 and 2703 nm wavelengths. The visible (800 nm) solar light and NIR (2703 nm) solar light can be separated using a chromatic aberration induced by the ball lens when the pinhole radius is 26 µm. 92.9% of the energy at the 800 nm wavelength (the intensity distribution hatched with the thin blue line) was used for daylight and 20.5% of the energy at the 2703 nm wavelength (the intensity distribution hatched with the bold red line) was used for TE generation. From the results of all the calculations at visible to NIR light wavelengths by the ray tracing method, it was found that the transparency of the visible light of 280–800 nm to the pair of pn junctions was 92.7%. 9.9% of the NIR light was estimated to be irradiated to generate electric power. Figure 3(b) shows the temperature distribution of the device surface. When the length of the TE elements was 374 µm from the radial position at 76 to 450 µm, the maximum temperature difference was estimated as 0.71 K.

### 3. Fabrication methods

Thin-film TEGs were fabricated using lithography and deposition processes. A schematic illustration of the fabrication process is shown in Fig. 4. A chemically amplified positive-tone photoresist (Tokyo Ohka Kogyo PMER P-CA1000PM) was spin-coated on the glass substrate. The thickness of the substrate was 200 µm. A p-type TE thin film of Bi$_2$Te$_2.7$Se$_{0.3}$ with a thickness of 1 µm was deposited on the substrate by a radio-frequency (RF) magnetron sputtering method. After that, the resist patterns were removed using acetone. N-type thin-film TE elements of Bi$_2$Te$_2.7$Se$_{0.3}$ with a thickness of 1 µm were also formed using the same process as the p-type thin-film TE elements. Then, thermal treatment was conducted at 623 K for 3 h in vacuum atmosphere to improve the crystallinity. To connect the thin-film TE elements, the resist patterns were formed and Cu thin films with a thickness of 500 nm were deposited by the sputtering method. A buffer layer of Cr with a thickness of 2 nm was used underlying the Bi$_2$Te$_2.7$Se$_{0.3}$, Bi$_2$Te$_2.7$Se$_{0.3}$ and Cu patterns. After the resist removal, a SiO$_2$ thin film with a thickness of 200 nm was coated onto the TE and Cu films. Finally, the resist patterns were formed to align the ball lenses, and then the ball lenses were put at the center of the TEGs with tweezers. The generated voltage of a pair of pn junctions was 216 µV/K, which was the average value at 303–323 K. The electrical conductivities of the TE films (10 × 0.5 mm$^2$) were 1250 S/cm (p-type) and 509 S/cm (n-type).

### 4. Results and discussion

#### 4.1 Fabrication of thermoelectric generators

Figures 5(a) and 5(b) show an optical microscopy image and a photograph of the TEGs with small ball lenses, respectively. The thin-film TE elements were electrically connected. The total electrical resistance (111 pairs of pn junctions) was 2.50 kΩ. The theoretical resistance calculated without the resistance of the contact and Cu electrodes was 1.84 kΩ using the resistivity of the TE and Cu thin films. This indicates that the resistance of the contact and Cu electrodes
can be estimated to be 0.66 kΩ. Here, the lenses were not fixed on the TEGs in order to evaluate the generation properties simply. However, it is also possible to fix the lenses by reflowing the resist for the alignment.

4.2 Evaluation of thermoelectric generators

The TE generation properties of the TEGs with ball lenses were evaluated. The electrical resistance of a serially connected one line consisting of seven TEGs was 158 Ω. Figures 6(a) and 6(b) show the generation properties when solar light (A.M.1.5) was irradiated at 298 K. The open-circuit voltage and maximum power were 0.88 mV and 1.0 nW, respectively. The temperature difference between the hot and cold sides (distance: 374 µm) was estimated as 0.58 K using the Seebeck coefficient of the thin-film TE elements. The open-circuit voltage and maximum power per unit area were 4.5 V/m² and 51 µW/m², respectively. The designed maximum power was 126 µW/m², which was calculated using the values of the electrical resistivity and Seebeck coefficients of the p- and n-type TE films, and the temperature difference between the hot and cold sides. The internal resistance of the fabricated TEG was 22.5 Ω, which was approximately 1.4 times larger than that of the designed one of 16.6 Ω. Furthermore, the generation voltage of the
fabricated TEG was 0.82 times the estimated one using the Seebeck coefficient of the TE films and the temperature difference. These results agreed with the reduction in generated power. Although the generated power was smaller than the designed one, the order of this generation power per unit area is sufficient for use in glass windows with a size of sub 1 square meter because a millivolt-ordered voltage can be charged to the battery.

5. Conclusions
Thin-film TEGs with small ball lenses were fabricated and evaluated. The design of the TEGs was conducted using the ray tracing method to calculate the solar light propagation and using FEM for heat conduction analysis. When the pinhole radius was 26 µm, the visible light transparency was estimated to be 92.7% for daylight, and 9.9% of the NIR light was estimated to generate the temperature difference of 0.71 K between the hot and cold sides. The electrical internal resistance of the fabricated TEGs was 2.50 kΩ. The open-circuit voltage and maximum generation power were 4.5 V/m² and 51 µW/m², respectively.

Acknowledgments
This study was partially supported by the Nanotechnology Platform Program (Micro–Nano Fabrication) of the Ministry of Education, Culture, Sports, Science and Technology, Japan, JSPS KAKENHI Grant Number 15K13845, and the Asahi Glass Foundation.

2) A. Zanella, N. Bui, A. Castellani, L. Vangelista, and M. Zorzi, IEEE Internet Things J. 1, 22 (2014).