Cooling-Free Infrared Sensors with Original Nanostructured Si-Ge Thermoelectric Material

Kotaro HIROSE*, Kyohei KAKUYAMA, Makoto MURATA, Masahiro ADACHI,
Yoshiyuki YAMAMOTO, and Tsunehiro TAKEUCHI

A thermopile, which is a type of cooling-free infrared sensor composed of thermoelectric materials, and detects infrared rays without using electric power. For making a high-performance sensor, we developed a germanium-silicon (Si-Ge)-based thin-film thermoelectric material. The thermal conductivity of the Si-Ge thermoelectric material was reduced to 1 $Wm^{-1}K^{-1}$ due to the artificial nano-structure in the materials. In addition, its Seebeck coefficient was effectively increased by co-doping. This paper demonstrates that the thermopile constructed using the developed nanostructured Si-Ge material successfully detects infrared rays, and a gases detection system using the thermopile detects methane in the ambient air.

Keywords: thermoelectric material, thermopile, nanostructure

1. Introduction

Infrared sensors are used in night-vision cameras, thermography devices, gas detectors, and various other devices. They are classified into two different types of device according to the principle of infrared detection: quantum infrared sensors, which directly absorb infrared rays using a semiconductor material, and thermal infrared sensors, which detect light by converting it into heat.[(1)-(4)] The former type devices have high sensitivity, but in principle require a cooling mechanism. Despite the slightly lower sensitivity, the latter has a big advantage in its cooling free structure. Because of this advantage, thermal infrared sensors are much suitable for use in mobile devices.

Thermal infrared sensors are further classified into two minor groups: bolometers[(2)] and thermopiles.[(3),(4)] A bolometer detects infrared rays using the temperature dependence of electrical resistivity in the materials used in the sensor. A small but finite amount of electrical power is constantly consumed in such devices to induce electrical current for the electrical resistivity measurement. In contrast, a thermopile detects the electric power generated by infrared rays without consuming external electrical power. However, thermopiles are inferior to bolometers in terms of sensitivity. Therefore, significant improvement in sensitivity is required for thermopiles.

The authors have developed thermoelectric materials possessing an improved sensitivity as thermopiles. As a result of intensive studies, we succeeded in developing a new, high-performance material simultaneously using two original technologies: nano-structuring[(5),(6)] and co-doping.[(7)-(9)] The developed material is characterized by a small thermal conductivity and superior performance in electrical properties, both of which are necessities of improving the sensitivity of thermopiles. In this paper, we briefly describe the development process of this nanostructured thermoelectric material, and then report the results of operation test of a thermopile and a gas detector.

2. Working Principle of Thermopiles

Figure 1 shows a schematic illustration (cross-sectional view) of thermopile. Infrared rays shed on the thermopile is converted into heat in the light-absorbing layer to generate a temperature gradient in the element. The integrated electrical field provides us with a certain voltage as a useful sensor. In this way, the thermopile detects the infrared rays.

The sensitivity S_v of a thermopile is expressed by the following formula:

$$S_v = N(|\alpha_p| + |\alpha_n|)\, R_{th} \fallingdotseq N(|\alpha_p| + |\alpha_n|)/\kappa,$$

where N represents the number of thermocouples; α_p and α_n represent the Seebeck coefficient*[1] of p-type and n-type thermoelectric materials, respectively; and R_{th} represents the thermal resistance of the thermopile. R_{th} is roughly inversely proportional to the thermal conductivity κ of thermoelectric material, though the minor contributions of the other parts of thermopile should be considered for the more precise estimation of R_{th}. This suggests that reducing thermal conductivity and increasing the Seebeck coefficient are of great importance for improving the sensitivity of thermopiles.

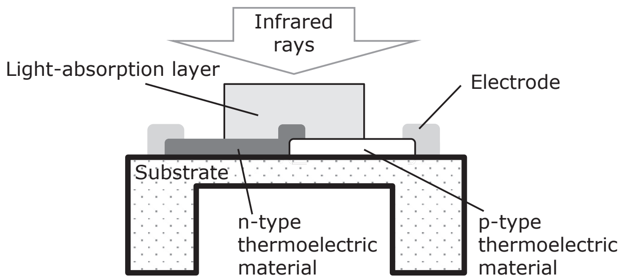

Fig. 1. Simplified schematic illustration of thermopile

3. Development for Nanostructured Si-Ge Thermoelectric Material

3-1 Comparison of thermoelectric materials

Figure 2 shows a comparison in room temperature properties between conventional thermoelectric materials commonly used for conventional thermopiles and the nanostructured Si-Ge thermoelectric material developed by our company.

Compared with the conventional materials, the new material has a lower thermal conductivity κ and larger absolute values of Seebeck coefficient $|\alpha_p|$ and $|\alpha_n|$. As a result of simple estimation of sensitivity, the values of $|\alpha_p|/\kappa$ and $|\alpha_n|/\kappa$ are 10 times or more higher than those of the conventional materials. This result indicates that the new material has the potential of achieving a sensitivity approximately 10 times higher than that of the other materials. The features of the new material are described in the subsequent sections.

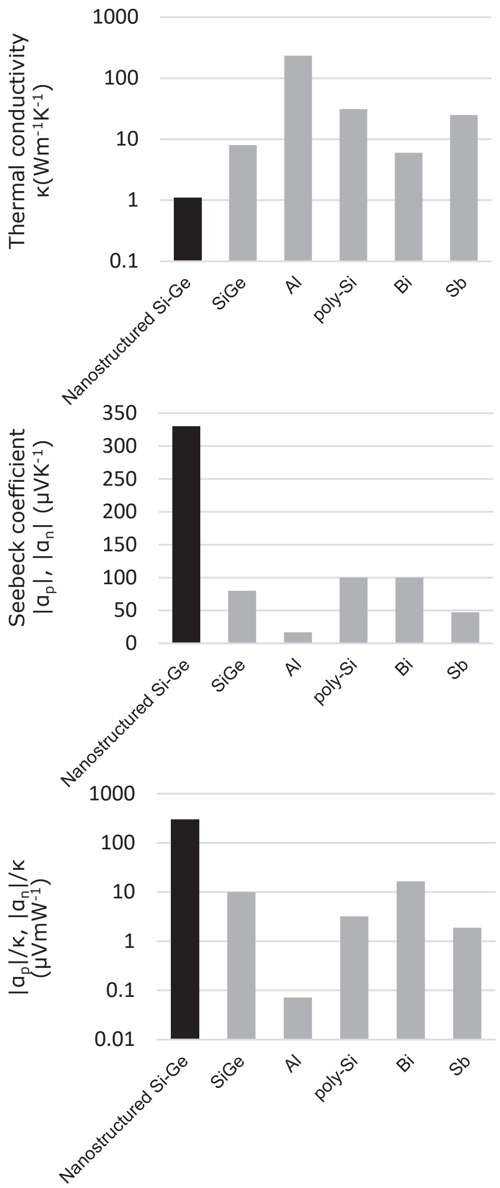

Fig. 2. Thermoelectric properties of each material at room temperature[(10)-(14)]

3-2 Reduction of thermal conductivity by nano-structuring

Thermal conductivity κ is generally expressed as $\kappa = \kappa_{el} + \kappa_{lat}$, where κ_{el} and κ_{lat} represent electron thermal conductivity and lattice thermal conductivity in association with phonons*2. The factor κ_{el} is reducible with increasing electrical resistivity of materials. However, increasing electrical resistivity deteriorates the other electrical properties (e.g. noise) of the thermopile. In this study, we focused on a significant reduction in κ_{lat}, which does not affect the electrical properties.

To reduce κ_{lat}, we introduced nano-structuring with which phonons are effectively scattered to reduce κ_{lat}.[(5),(6),(15)-(17)] Nanostructures such as superlattices,[(15)] nanowires,[(16)] and quantum dots[(17)] have been frequently employed. For example, a paper reports that the thermal conductivity of a PbTe-based material was effectively reduced from κ = 4.5 $\mathrm{Wm^{-1}W^{-1}}$ to κ = 2.0 $\mathrm{Wm^{-1}W^{-1}}$ by forming nanostructures with the addition of Ge.[(18)] We used a unique nanostructure formation technique in which nanocrystals are precipitated in amorphous material and homogeneously distributed over the whole sample, and succeeded in effectively enhancing phonon scattering.[(5),(6)] The volume fraction of nanostructure and consequently the lattice thermal conductivity are easily controlled by the annealing condition. This characteristic is the big advantage over the previously reported techniques.

A cross-sectional TEM image of the fabricated new material is shown in Fig. 3. The areas where atoms are periodically aligned are surrounded by white dashed lines. These areas indicate nanocrystals, and outside of these areas is the amorphous phase. Together with the random structure in the amorphous phase, a large number of grain boundaries of the nano-crystals effectively increase the probability of phonon scattering to effectively decrease κ_{lat}.

Figure 4 shows the averaged grain size dependence of κ. The reduction of mean grain size of nano-crystals natu-

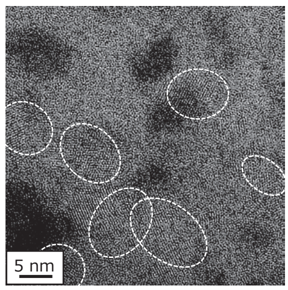

Fig. 3. Cross sectional TEM image of nanostructured Si-Ge

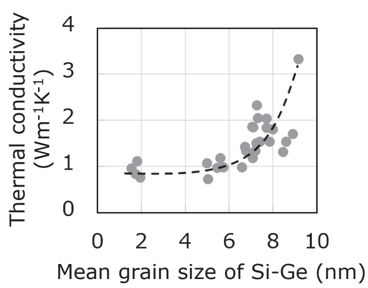

Fig. 4. Relationship between nanocrystal grain size and thermal conductivity[(6)]

rally reduced mean free path of phonons to decrease thermal conductivity, κ. Very tiny thermal conductivity less than 1 $Wm^{-1}W^{-1}$ is obtained in our newly developed materials when the averaged grain size stays below 6 nm. This magnitude of thermal conductivity is approximately one-eighth that of conventional crystalline Si-Ge materials.[(5), (6)]

3-3 Improvement of electrical properties by co-doping

It is known that electrical properties, such as Seebeck coefficient α, depend on an electronic structure such as the density of states*3 and the group velocity near the Fermi level E_F (within ±3 k_BT, where k_B represents the Boltzmann constant).[(7),(8)] With the aim of artificially controlling the electronic structure, we developed a co-doping technique. In co-doping, α is improved by adding an element having two different roles: forming a characteristics in the density of states (such as a new peak in association with the energy level of impurity elements) and adjusting the Fermi level to optimize the electron transport properties. We screened elements by means of electric structure calculations, and selected Au for forming the new energy levels and B to adjust the Fermi level. The α-value of this material was increased to 330 μVK^{-1} by co-doping Au and B at optimum concentrations.

4. Use of Originally Developed Material for Thermopile

4-1 Verifying the principle of function: detection of infrared rays

A prototype thermopile was fabricated using the newly developed material (see Fig. 5). Then, a simple test was carried out to verify the function of the prototype device by shedding infrared rays on it. The results are shown in Fig. 6.

The prototype device was exposed to the infrared rays for 20 to 40 seconds, and an output voltage of approximately 0.7 mV was stably generated during the irradiation. The evaluated time constant are shown in Fig. 7. The time constant was 42 ms, which was equivalent to that of conventional thermopiles.

Fig. 5. Appearance of the prototype device

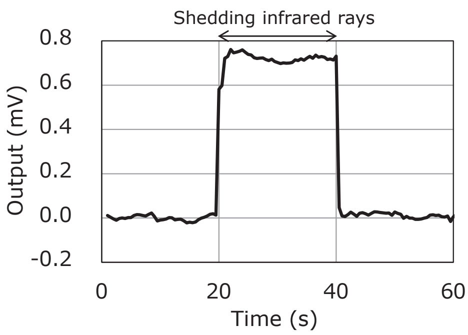

Fig. 6. Detection of infrared rays with prototype thermopile

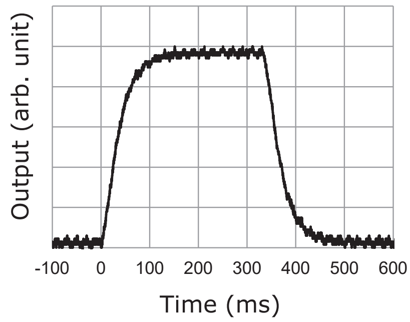

Fig. 7. Evaluation of time constant

4-2 Verification of gas detection

Infrared ray sensors are generally combined with an infrared laser light source to detect a gas. As is well known, each type of gas has its own light absorption range of wavelength.[(19)] For example, infrared rays can be used to detect NOx, methane, and water vapor contained in vehicle emissions.

In combination with quantum cascade lasers[(20)-(23)] made by our company, we constructed a measurement system as shown in Fig. 8, and measured the concentration of methane in the atmospheric air. The measurement results are shown in Fig. 9.

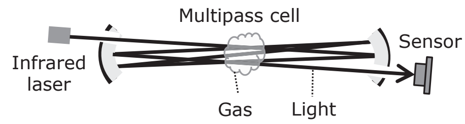

Fig. 8. Gas detection system

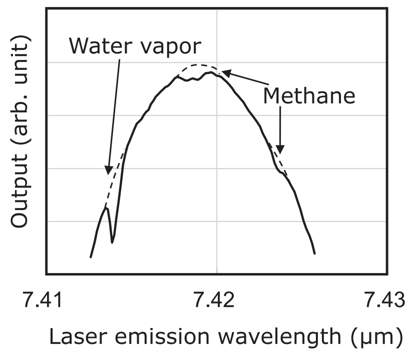

Fig. 9. Detection of methane in the atmospheric air

The figure indicates that the laser is absorbed by water vapor and methane (1 ppm) in the atmospheric air. It was also confirmed that the test results showed good consistency with the laser transmittance calculation for each wavelength at 1 ppm methane in a nitrogen atmosphere.

These results verified that the nanostructured Si-Ge thermoelectric material is usable in thermopiles.

5. Conclusions

A nanostructured Si-Ge thermoelectric material that was newly developed to improve the sensitivity of thermopiles. The performance of the new material was enhanced by means of nano-structuring and co-doping. The function of a thermopile constructed of the new material was evaluated by a typical test. As a result, it was verified that the developed thermopile is capable of detecting infrared rays and also even a small amount of methane (1 ppm) when this sensor is combined with an infrared laser.

In the future, we will improve and optimize the thermopile design in order to make full use of the potential of the new material and fabricate a highly sensitive thermopile.

Technical Terms

*1 Seebeck coefficient: Assume that a temperature difference ΔT in a material will generate a voltage ΔV at both ends of the temperature difference. Then, the Seebeck coefficient of the material is given by $-\Delta V/\Delta T$. In other words, a Seebeck coefficient is a physical quantity specific to a substance that represents the magnitude of the voltage generated by a temperature difference.

*2 Phonon: A vibration is considered to be an assembly of particles having an energy corresponding to the vibration frequency. The particles are called phonons.

*3 Density of states: A physical quantity that represents the extent to which electrons with a certain energy can exist in a material.

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Contributors The lead author is indicated by an asterisk (*).

K. HIROSE*
• Transmission Devices Laboratory

K. KAKUYAMA
• Transmission Devices Laboratory

M. MURATA
• Doctor of Science
Transmission Devices Laboratory

M. ADACHI
• Doctor of Engineering
Group Manager, Transmission Devices Laboratory

Y. YAMAMOTO
• Department Manager, Transmission Devices Laboratory

T. TAKEUCHI
• Doctor of Engineering
Professor, Toyota Technological Institute