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【論文の内容の要旨】

Thermoelectric conversion, which can convert heat into electricity, has been attracting attention as energy harvesting technologies to utilize the environmental waste heat as a new energy source. To progress thermoelectric conversion technology, we must develop the materials with high conversion performance in combination with safety and low cost. Dresselhaus et al. theoretically proposed that one-dimensional (1D) materials with nanostructures have the potential to exhibit the highest thermoelectric performance due to the reduction of thermal conductivity and the quantum confinement effect. The enhancement by the former factor has well been demonstrated; however, the experimental verification of the latter property in 1D systems has not been proved yet. The clarification of this prediction will lead to creating a new approach for improving thermoelectric performance, which has not been accomplished with conventional thermoelectric materials.

Here, this paper aims to clarify the relationship between the electronic structure of 1D systems and their thermoelectric properties. We experimentally investigated the thermoelectric properties of films of single-walled carbon nanotubes (SWCNTs), which are ideal 1D materials. The chemical potentials of high-purity semiconducting and metallic SWCNTs were continuously varied using an ionic liquid-based electric double layer carrier injection method. As a result, we clarified the unique thermoelectric properties of semiconducting and metallic SWCNT films due to their 1D electronic

structure, respectively.

This paper is composed of the following six chapters.

Chapter 1 describes the background and purpose of this study.

Chapter 3 describes the development of a new separation technique for single-chirality SWCNTs. The sample purity of SWCNTs is crucial to observe the one-dimensionality. However, conventional separation techniques using surfactants could not altogether remove the residual few percent of metallic SWCNTs in semiconducting single-chirality SWCNT separation. Here, we developed a new technique to obtain high-purity (>99%) single-chirality SWCNTs by improving a reported gel chromatography separation to precisely control the acidity, or pH, as an additional parameter. The pH-controlled method succeeded in completely removing the residual metallic SWCNTs because metallic and semiconducting types have different sensitivities in responding to changes in pH. The high-purity sample obtained in this chapter was used for thermoelectric measurements in the next chapter and later, enabling the series of this study to be unique.

Chapter 4 systematically demonstrates the thermoelectric properties of high-purity semiconducting and metallic SWCNTs, and their mixtures. We observed the enhancement of thermoelectric performance due to the 1D electronic structure by adjusting the chemical potential of metallic SWCNTs at the vicinity of van Hove singularity (vHs). The enhancement was manifested in a simultaneous increase in electrical conductivity and the Seebeck coefficient. In conventional materials, there is a trade-off relationship between electrical conductivity and the Seebeck coefficient, which means that the increase of electrical conductivity induces a decrease of the Seebeck coefficient. However, the metallic SWCNTs violated the trade-off, demonstrating that the 1D electronic structure can enhance the thermoelectric performance due to the quantum confinement effect. Furthermore, we experimentally showed that the electrical conductivity increased without decreasing the Seebeck coefficient by preparing macroscopically aligned metallic SWCNT thin films, indicating that the morphology control of SWCNT samples can lead to further performance improvement.

Chapter 5 identifies the traces of thermoelectric properties due to the 1D electronic structure in semiconducting SWCNTs. Using a simple model based on the Boltzmann transport equation, we showed that it is difficult to identify the 1D traces in the Seebeck coefficient and the power factor, the typical thermoelectric parameters. However, the L_{12} term, thermoelectrical conductivity term, was expected to reflect the dimensionality of the materials. In particular, the 1D electronic structure was expected to have a peak structure in L_{12} at the vHs as a function of the chemical potential. Here, we observed the

peak structure in L_{12} on high-purity semiconducting SWCNTs thin films, consistent with the theoretical prediction. The linear response theory analysis and the experimental results of 2D semiconductors supported that the peak is a 1D trace originating from the electronic structure of SWCNTs. In the 1D system, the L_{12} term shows the peak structure in the low electrical conductivity region. We could understand the advantage of 1D materials as high thermoelectric performance materials from such behavior.

In Chapter 6, the conclusions obtained in this thesis are summarized.

The present study systematically investigated the fundamental properties concerning the relationship between the 1D electronic structure of SWCNTs and their thermoelectric properties in their thin films. The enhancement of thermoelectric properties due to the 1D nature of metallic SWCNTs is in a simultaneous increase in electrical conductivity and the Seebeck coefficient. We demonstrated that the 1D electronic structures violate the trade-off problem of conventional thermoelectric materials and improve thermoelectric performance. On the other hand, the one-dimensionality of semiconducting SWCNTs can be identified in the thermoelectrical conductivity term, L_{12} term. The relationship between electronic structure and thermoelectric properties can be observed in L_{12}, which would be a good metric for evaluations of thermoelectric performance in low-dimensional materials. The author believes that the knowledge of the thermoelectric properties of 1D materials obtained in this study contributes to investigating the fundamental physics and provides a scheme for creating new energy conversion technologies that could not be achieved with existing inorganic thermoelectric materials.