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## Resistivity and Seebeck coefficient measurements of a bismuth microwire array

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#### Abstract

The resistivity and Seebeck coefficient of a bismuth microwire array (wire diameter:  $25 \mu m$ ) were successfully measured from 25 to 300 K. To eliminate the influence of the contact resistance between the wire edges of the microwire array and copper electrodes, the titanium (100 nm)/copper (500 nm) film layers were deposited as interlayer on the wire edge by ion plating method. Copper electrodes were glued by using Pb–Sn solder. The resistivity and the Seebeck coefficient at 300 K were approximately  $1.8 \times 10^{-6}$  Om and  $-54 \times 10^{-6}$  V/K, respectively. The value of the resistivity and the Seebeck coefficient were in good agreement with those of bulk polycrystalline bismuth reported previously. Thus, the effects of the contact resistance for the microwire array were almost resolved, and the chemical reaction of the Pb–Sn solder and bismuth was prevented by using the thin-film layer. The technique is expected to be applicable to nanowire arrays as well.

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### 1. Introduction

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The performance of a thermoelectric material is expressed by the figure of merit Z, which is a function of the Seebeck coefficient  $\alpha$ , the resistivity  $\rho$ , and the thermal conductivity  $\kappa$  [\[1\]](#page--1-0). Recently, thermoelectric materials with low-dimensional

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structures, for example superlattices and nanowire, were proposed to enhance the figure of merit [\[1–3\]](#page--1-0). The application of an external magnetic field enhances the figure of merit of bismuth-based materials more than twofold because the magneto-Seebeck coefficient for an optimum magnetic field under 0.5 T, which is achievable in real applications, increases by a factor of 1.5 [\[4\]](#page--1-0). The magneto-Seebeck coefficient has been shown to be dependent on the shape of the sample (the geometry effect), which is disadvantageous for bulk samples due to the low-aspect ratio [\[5\]](#page--1-0). Our group has investigated the magneto-Seebeck coefficient by using a bismuth microwire array with a highaspect ratio in order to enhance the figure of merit by eliminating the geometry effect. As a result, the magnetic field dependence and increasing ratio of the measured magneto-Seebeck coefficient were, qualitatively and quantitatively, in good agreement with calculated results [\[6\].](#page--1-0)

On the other hand, the resistivity, which is a parameter of the figure of merit [\[1\]](#page--1-0), was hardly reported using thermoelectric material introduced a wire-array structure. In many cases, only the resistance of the nanowire array was represented instead of the resistivity [\[7–9\].](#page--1-0) Even when the resistivity was estimated, it was much larger than that of bulk single-crystal or polycrystalline bismuth [\[10–12\]](#page--1-0). The wire edge of the nanowire array (a diameter of the wire is on the order of nanometer) is complex structure due to the amount of the wires. It is easy to contain the contact resistance between edges of all the wires and electrodes in the value of the measured resistance. In fact, the typical resistance of the nanowire-array sample was more than  $1\Omega$ , and influence of the contact resistance must be considered [\[7,9,13\].](#page--1-0) With the nanowire array sample, it is difficult to discriminate whether the value of the resistance derived from the quantum effect or contact resistance.

Recently, our group investigated the properties of several silver pastes and Pb–Sn solder as a binder for thermoelectric materials, in order to eliminate the contact resistance [\[14\]](#page--1-0). As another possible option, for the first time, a method to attach the microwire array to the electrodes was introduced by using a thin-film layer deposited by ion plating in order to reduce the contact resistance. The microwire-array sample was used to neglect influence of the quantumeffect and suitable to investigate the influence of the contact resistance. In this study, the techniques to reduce the contact resistance between the wire-array sample and electrodes were described. Then comparison of the resistivity with that of bulk polycrystalline bismuth sample was attempted because the estimation of only contact resistance was difficult.

#### 2. Experimental techniques

A high-purity polycrystalline bismuth ingot by floating zone method (6N grade) was prepared for the experiment. Bulk sample was cut from the ingot and the surface of the bulk sample was closely polished. The copper electrodes were glued to the edge of the bulk sample by using the silver nanopaste. On the other hand, the bismuth microwire array was fabricated by a high-pressure injection method using a glass-capillary plate as a template (length, 1 mm; pore diameter,  $25 \mu m$ ; pore density of the plat, 55%) [\[15\],](#page--1-0) not expecting the quantum effect due to much lager diameter than that of mean-free path of phonons [\[16\].](#page--1-0) In the ion-plating process, in order to deposit a thin film, a substrate fixed the microwire-array sample attached was set 500 mm away from the crucible at room temperature. Titanium shots (nominal purity 99.9%, diameter 5 mm, length 5 mm) and copper shots (nominal purity 99.9999%, diameter 5 mm, length 10 mm) were placed in the crucible. The base pressure was on the order of  $10^{-4}$  Pa. Argon gas was then introduced until the pressure increased to a level on the order of  $10^{-2}$ Pa. An argon plasma was generated by radio frequency (RF) electric power (power 100 W, frequency 13.56 MHz), which was applied by a spiral coil set 300 mm away from the substrate. A bias voltage of 100 V was applied to the substrate using a power supply. Under these conditions, titanium film was deposited to the wire edges of the microwire-array sample by an electron beam directed into the crucible, and the growth rate monitored by a quartz oscillator was 1 nm/s, and

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