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An Alternating-Current Voltage Modulated Thermal Probe Technique for Local Seebeck Coefficient Characterization *

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An ac voltage-modulated thermal probe technique based on the atomic force microscope is developed to measure local Seebeck coefficients (S) of thermoelectric bulk and films. The characterization principle is based on the strictly quadratic relationship between the excited local dc Seebeck voltage and the applied ac voltage at high frequency. Excellent agreement is found between local S values and their corresponding macro-S values of thermoelectric bulk and thin films. This thermoelectric probe technique provides a very convenient, promising tool for local thermoelectric parameters with sub-micrometer scale resolution.

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Nanostructured and nanocomposite thermoelectric materials have recently attracted a great deal of attention due to the optimization of thermal and electrical transports for high thermoelectric performance.[1–6] The initial ideas for the applications of nano-structures in thermoelectric materials are that the lattice thermal conductivity can be depressed by the scattering of nano-particles or nano-boundaries as well as the enhanced electron density of states at the Fermi level. The latter is expected to enhance Seebeck coefficients due to the fact that the low energy carriers can be filtered by nano-sized grain boundaries. Lowered thermal conductivity and enhanced thermoelectric figure of merit have been observed in lots of bulk materials with nanostructures or nano-impurities. However, the thermal and electrical transports in these nano-materials are usually measured by normal commercial systems, in which only the statistical values of the transports are obtained. The characterization of local thermoelectric parameters still remains a challenging task at the submicro, even nanometer level. Scanning probe microscopy, as a powerful tool for nanostructure imaging and local properties characterization, has become a promising technique for measuring local thermal and electrical properties, like scanning tunneling microscopy,[7] scanning thermal microscopy,[8] and scanning Joule expansion microscopy.[9] Recent work has demonstrated simultaneously determined the thermal conductivity and Seebeck coefficient of Bi_2Se_3 thin film by a microprobe technique.[10]

For local Seebeck coefficient (S) measurement, it is necessary to know the exact temperature variation, which induces a Seebeck voltage in thermoelectric materials. Thus in previous works, temperature variation was directly calculated for local S values based on the heat transfer model describing the heated probe-sample junction.[10] However, this model is still complicated for general application in measuring local S values. Thus it is very important and necessary to develop a more simple and more efficient method for measuring the local Seebeck coefficient. In the present study, one ac voltage modulated-thermal probe technique is presented for measuring local S values based on the commercial atomic force microscopy. This technique avoids directly calculating the necessary temperature differences, and provides a very convenient approach for determining the local, even nanoscale, Seebeck coefficient.

The schematic diagram of the thermal probe technique on the commercial atomic force microscope (SPA 400, SPI3800N, Seiko Inc. Japan) is shown in Fig. 1. The thermal probe is the so-called Wollaston wire (5-μm-diameter Pt-Rh core cladded with a 75-μm-diameter silver shell), acting as the local heater, thermometer and voltage electrode during its contact with the sample surface. When an ac voltage ($V_0 \sin \omega t$) is applied to the thermal probe, it will give rise to a temperature rise (ΔT) on the tip by the electrical power ($P_{2\omega}$) due to the Joule effect. Theoreti-

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cally ΔT will vary with 2ω ($T_{2\omega}$), including ac and dc components. However, if the excitation frequency of the ac voltage is high enough that the amplitude of the temperature oscillations (ac component) could be negligible, and the dc temperature variation ($\Delta T^{\rm dc}_{\rm sample}$) above the ambient environment dominates, which results in a dc Seebeck voltage ($V^{\rm dc}_{\rm Seebeck}$) between the heating region and non-heating region of the sample, i.e., $V^{\rm dc}_{\rm Seebeck} = S \cdot \Delta T^{\rm dc}_{\rm sample}$.

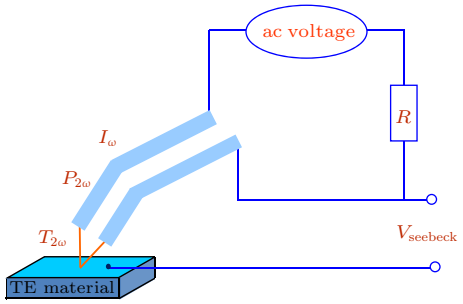

Fig. 1. The schematic diagram of the ac voltage-modulated thermal probe measurement for the local Seebeck coefficient based on the commercial atomic force microscope.

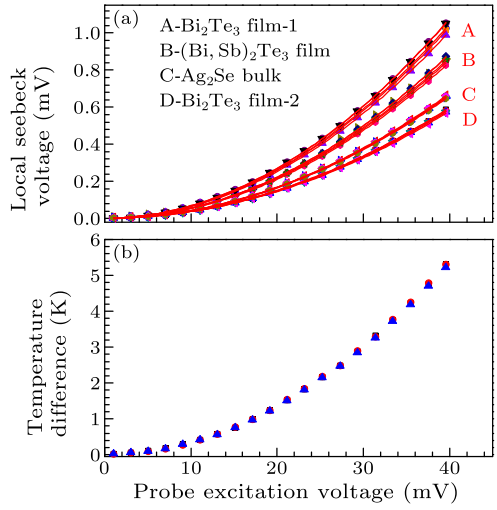

Fig. 2. (a) Local Seebeck voltage signal at different excitation voltages for Ag_2Se thermoelectric bulk, Bi_2Te_3 film-1, Bi_2Te_3 film-2 and $(Bi, Sb)_2Te_3$ thermoelectric thin films, and (b) the temperature difference as a function of probe excitation voltage for the Ag_2Se bulk reference sample. Note that for Ag_2Se bulk, Bi_2Te_3 films, their negative signs of the local Seebeck voltage are omitted.

According to the Joule effect, $\Delta T^{\rm dc}_{\rm sample}$ induced by the electric power should be in proportion to the square of the excitation voltage (V_0), i.e., $\Delta T^{\rm dc}_{\rm sample} \propto V_0^2$, thus $V^{\rm dc}_{\rm Seebeck}$ also has a similar relation with V_0, i.e., $V^{\rm dc}_{\rm Seebeck} \propto V_0^2$. This is very important for our local Seebeck coefficient measurement, in which the local Seebeck coefficient measurement could be transferred into the correlation of $V^{\rm dc}_{\rm Seebeck}$ and V_0^2, i.e., $V^{\rm dc}_{\rm Seebeck} = S \cdot \Delta T^{\rm dc}_{\rm sample} = k \cdot S \cdot V_0^2$, where k is a constant. Thus we can obtain local S values in comparison with that of the reference sample. In our measurement, the ac voltage is applied by the function generator (Agilent 3301), while the dc Seebeck voltage was detected by the digit precision multimeter (Tektronix DMM4050). Thermoelectric Ag_2Se bulk, Bi_2Te_3 films and $(Bi, Sb)_2Te_3$ films are used for local measurements with the same contact force during the AFM operation.

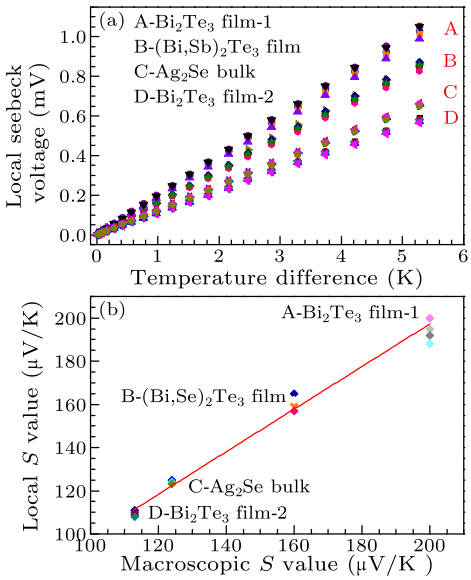

Fig. 3. (a) Local Seebeck voltage of thermoelectric samples as a function of temperature rise, (b) the calculated local Seebeck coefficient values in comparison with the corresponding macroscopic values. Note that for Ag_2Se bulk, Bi_2Te_3 films, their negative signs of the Seebeck voltage and S values are omitted.

We firstly measure the excitation voltage dependence of local dc Seebeck voltage for thermoelectric samples as shown in Fig. 2(a). The measured specimens include Ag_2Se bulk, $(Bi, Sb)_2Te_3$ film and two Bi_2Te_3 films (Bi_2Te_3 film-1, Bi_2Te_3 film-2). The difference between Bi_2Te_3 film-1 and Bi_2Te_3 film-2 lies in their difference of the macroscopic Seebeck coefficients, $-200\,\mu$V/K for the former and $-113\,\mu$V/K for the latter. Figure 2(a) gives local measurement data of five different locations. Their local Seebeck voltage signals show a strictly quadratic relationship with high frequency ac voltage, which is in excellent agreement with the fitted theoretical considerations, i.e., $V^{\rm dc}_{\rm Seebeck} \propto V_0^2$. For understanding the temperature rise behavior excited by the ac voltage, a Ag_2Se bulk sample is taken for reference calibration due to its very homogeneous local Seebeck voltage. For bulk Ag_2Se, its macroscopic S value of $-124\,\mu$V/K was used to calculate the temperature rise above ambient ($\Delta T^{\rm dc}_{\rm sample}$) at different ac voltages, as shown in Fig. 2(b). It is obvious that $\Delta T^{\rm dc}_{\rm sample}$ also follows very quadratic behavior with the applied ac voltage V_0, as the above-mentioned $V^{\rm dc}_{\rm Seebeck} \propto V_0^2$. As a result, we can further calculate the local S value based on the ob-

tained temperature variation $\Delta T^{\rm dc}_{\rm sample}$ of the reference Ag_2Se bulk. Figure 3(a) gives the local Seebeck voltages of the samples as a function of the temperature rise. A good linear correlation between $V^{\rm dc}_{\rm Seebeck}$ and $\Delta T^{\rm dc}_{\rm sample}$ is clearly observed, as indicated by the fitted line. The slope $dV^{\rm dc}_{\rm Seebeck}/d\Delta T^{\rm dc}_{\rm sample}$ is used for calculating local S values. For the Bi_2Te_3 film-1, Bi_2Te_3 film-2 and (Bi, Sb)$_2$Te$_3$ films, their local S values are averaged $-195\,\mu$V/K, $-110\,\mu$V/K, $+162\,\mu$V/K, respectively, which are very close to those corresponding macroscopic S values $-200\,\mu$V/K, $-113\,\mu$V/K, $+160\,\mu$V/K. Figure 3(b) gives a comparison of the local S value with their macro-S values. The good agreement validates the feasibility and the accuracy of this method.

The present ac voltage modulated thermal probe technique provides a very simple and convenient approach for local Seebeck coefficient. The spatial resolution of such a thermal probe technique is dependent on the thermal exchange radius between the thermal tip and the sample. It was around 200 nm estimated by Lefèvre *et al.*,[11] which implies that the present technique for the local Seebeck coefficient could reach a sub-micrometer spatial resolution.

In summary, an ac voltage-modulated thermal probe technique based on the atomic force microscope has been developed to measure local Seebeck coefficients of thermoelectric materials. The characterization principle is based on the strictly quadratic relationship between the excited local dc Seebeck voltage (or temperature rise above ambient) with the applied ac voltage. Excellent agreement is found between the local S values and the corresponding macro-S values. Such a thermoelectric probe technique provides a very convenient, promising tool for local thermoelectric parameters with sub-micrometer scale resolution.

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