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The size-dependent thermoelectric response of tungsten-constantan thermocouple in the sub-micro scale

Zhenyu Cui · Jianfei Sun · Changling Wang · Can Li · Ning Gu

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Abstract We present the behavior of the thermoelectric response in a nanoscale tungsten-constantan (Cu 58%, Ni 42%) thermocouple (TC). The TC is tip-section typed and fabricated by the stepping method. The thermal electromotive force (emf) showed nearly linear behavior versus temperature over the range from 0 to 100°C. For the thermocouples with contact radius below 300 nm, the Seebeck coefficient decreased with the size of thermocouples turning smaller. According to the theory based on the free-electron model, the size-dependence thermal electric response may be ascribed to the change of electronic property in nanoscale.

1 Introduction

Temperature, derived from other thermodynamic parameters such as heat, energy, heat capacity and etc. [1, 2], has very important significance in the biomedical field. The cellular activity is greatly influenced by temperature and cells can only remain effective in narrow limits of temperature. Enzyme systems show different efficiency as temperature varying within a narrow range. Also, lesions of normal cells can be reflected from tiny change of temperature. Thermocouples, which were based on Seebeck effect, have been extensively used to measure the temperature. With the increasing research interests on single-cell and sub-cell, the size of TC is turning into nanoscale. However, there have been few reports on the investigation of thermoelectric response of TCs in nanometer scale.

In this article we present the experimental results of size-dependent thermal electromotive force (emf) in the tip-section structured thermocouples. We made tip-section thermocouples of different sizes by control of contact area. The experimental results show that the Seebeck coefficient is dependent on the contact radius of tip, meaning that the size effect exists in a nanoscale heterojunction. The sharp W tip, fabricated by the electrochemical etching method was moved to a Cu–Ni alloy section under the precise control of PI system (E-710, PI Co, Germany). The PI system can realize the minimum incremental motion of subnanometer and the minimum responding time of one microsecond. Accurate gap-spacing can be indicated by the signal transduction between the tip and substrate.

A temperature between two points in a conductor or semiconductor results in a voltage difference between these two points. This phenomenon is called the Seebeck effect [3]. The thermoelectric voltage developed per unit temperature difference in a conductor is called the Seebeck coefficient. According to Mott and Jones, the Seebeck coefficient of a pure metal (bulk) is given by the free-electron model as

$$S_B = -\frac{\pi^2}{3e}\frac{k^2 T}{\zeta}\left[\left(\frac{\partial \ln l}{\partial \ln E}\right)_{E=\zeta} + 1\right], \tag{1}$$

where l is the mean path of carriers, E is the electron energy, ζ is the Fermi energy, k is the Boltzmann constant and T is the absolute temperature. According to (1), as the Fermi energy and the electron energy is constant in a macroscopic solid, Seebeck coefficient is affected only by the type of conductor together with the temperature. It is normally considered as a constant in a specified range of temperature.

Z. Cui · J. Sun · C. Wang · C. Li · N. Gu (✉)
State Key Laboratory of Bioelectronics, Jiangsu Key Laboratory for Biomaterials and Devices, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210009, China
e-mail: guning@seu.edu.cn
Fax: +86-25-83272460

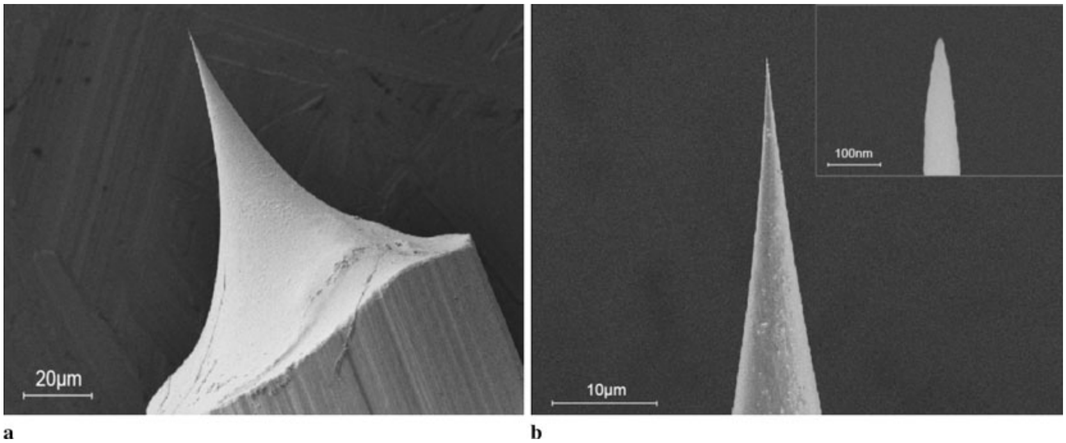

Fig. 1 SEM images showing a sharp W tip. (**a**) 1,000× magnification. (**b**) 5,000× magnification. The *inset*: 300,000× magnification

However, a size effect had been found in the thin-film thermocouples [4–7]. For a pure metal film, the electronic thermopower was proved to be inverse proportional to the film thickness t. This result indicated the existence of a size effect in thin film. Compared with the thin-film typed thermocouple, the tip-section typed thermocouple has more reality in the practical biomedical applications. However, the research of size effect in the tip-section typed thermocouple has not been reported.

2 Experimental procedures

2.1 Preparation of nanoscale W tips

The W tip was prepared from a tungsten wire (0.30 mm diameter, 99.95%), electrochemically etched using a drop-off technique developed by Bryant et al. [8, 9]. 3 M NaOH was chosen as the etchant solution. When the solution level was above the end of W wire, the etch current considerably reduced. We designed a detection circuit, which used the change of current at drop-off point as a relay to stop the electrochemical etching. The circuit had a minimum cut-off time of about 500 ns. This guaranteed sharpness of the tips. Figure 1 showed a typical SEM image of W tip. The approximate radius of curvature (ROC) for the tip shown was 20 nm. The corresponding cone angle was 12°. By the statistic of more than 40 tips, the average ROC was 20 ± 4 nm and the average cone angle was $12 \pm 2°$.

2.2 Preparation of W–CuNi heterojunction

The constantan cross-section was immobilized on a three-dimension micro-positioning platform, used as the cathode. Meanwhile, the W tip was fixed to a piezo-driven nano-positioner with an L-mould linkage mechanism and connected with the power source. The tip was used as the anode and examined via a charged coupled device (CCD) microscope (NCC320A type).

The whole contact process (Fig. 2, part B) was executed in a Bakelite tube (5 mm in diameter and 40 mm in length). Constantan substrate and tungsten tip were adjusted in a common plane by regulating the micro-positioning platform. Before the stepping process started, W probe was held coaxially in a Bakelite tube (0.5 mm in diameter and 20 mm in length), 20 μm away from CuNi alloy surface. The tip can move at an adjustable speed from 20 nm/step to 100 nm/step with the control of PI system. Before every stepping, ammeter detected the loop current and fed back. If the result was below 10 μA, PI system received a "yes" and the stepping process continued. The detection was repeated in every 50 microsecond until the tip contacted the plane (once the contact finished, the current would be about 5 mA). After the tip and the section contacted, the adhesive was dripped into the Bakelite tube and the position of the probe was ultimately fixed.

2.3 Measurement of Seebeck coefficient

The thermocouples were calibrated in the temperature range of 0–100°C. The temperature of the heating system was measured with an indicator (Type-K thermocouple). The emf was measured with a digital multimeter (HP model 34410A). The reference thermojunction was immersed in a large reservoir filled with crushed ice during the measuring process. The thermocouple connection was made with extension wires of the same material.

3 Results and discussions

In order to study the size effect of thermocouples, we set different stepping distances (from 20 nm to 100 nm) to control the size of junction. In the moment that the W tip only

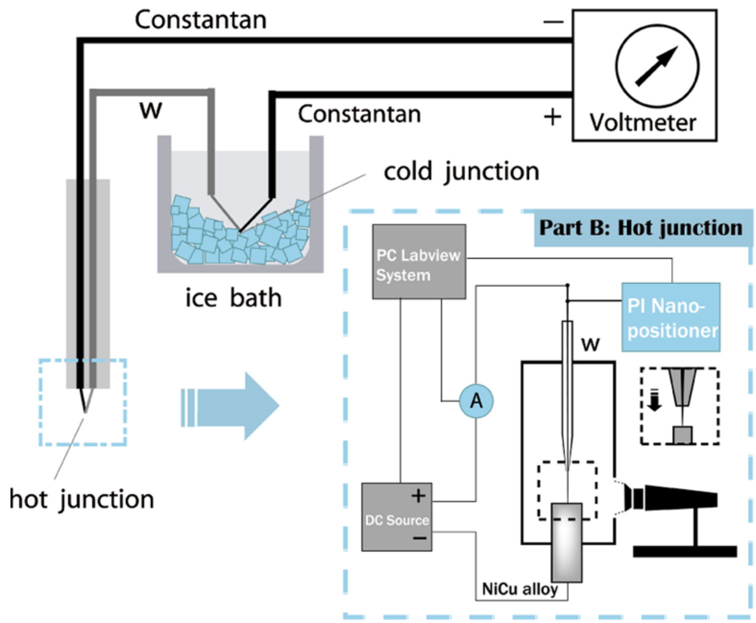

Fig. 2 The schematic diagram for connection of a thermocouple to reveal the hot junction, cold junction, reference temperature and the voltage difference of the couple. The block *inset* is the experimental setup of W–CuNi heterojunction, working as the hot junction

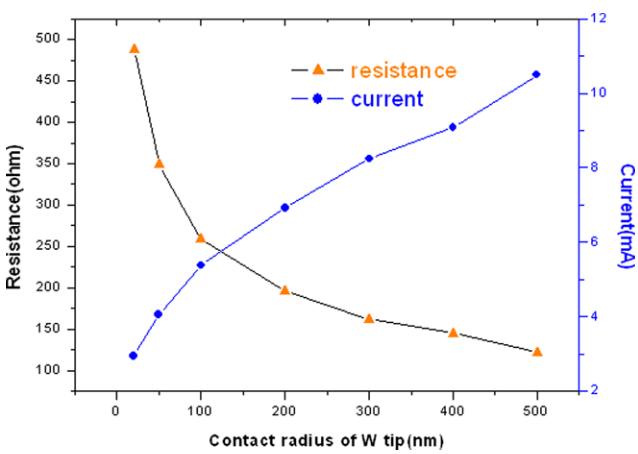

Fig. 3 Current and resistance of thermocouple vs. contact radius of W tip–CuNi section

just contacts the Cu/Ni alloy section, the resistance is to generate a leap from approximate infinity to a finite value. We set this point as start-point, meaning the contact area is too small to be neglected. Then the tip was driven to proceed as 50 nm/step or 100 nm/step. Because the tip is very sharp and the hardness of the tip is much larger than that of the Cu/Ni alloy, the tip will extrude the section to form a conical-shaped contact area. We can define the bottom radius of the conical-shaped contact area as the contact radius. Because the conical angle of the tip is 12° ($\cos(6°) = 0.994$), the bottom radius of the conical-shaped contact area is approximately one tenth of the stepping distance. Thus, the contact radius can be estimated by calculating the recorded stepping distances. The variations of current and resistance with contact radius were shown in Fig. 3. As expected, the resistance increased with the junction size decreasing. In this way, the value of resistance can indicate the contact status of W probe.

The thermal emf versus temperature of thermocouples with different dimensions was shown in Fig. 4a. In the temperature range of 0–100°C, the nearly linear curves can be observed in all cases. The slope of the plots shown in Fig. 4a equals the Seebeck coefficient. The Seebeck coefficient S as a function of the contact radius r was also showed in the inset. The continuous line was the best fit to the experimental results. Figure 4b showed the Seebeck coefficient of one thermocouple during heating and cooling process. No detectable hysteresis in these measurements was discerned.

The bulk value of S for these two metals is 36 μV/°C. As the decrease of junction size, S reduces to 30 μV/°C, 16.7% lower than the expected value. The experimental results indicate that the Seebeck coefficient has an obvious decrease as the size of thermocouples turned smaller. It can be seen that S is approximately constant when the contact radius is larger than 300 nm, reaching a maximum value at $S = 36.2$ μV/°C.

In fact, the bands of solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest-neighbor interactions, and the Fermi level can be considered continuous. However, at small sizes, the Fermi level lies between two bands and it may become discrete [10]. Also, it is realized that in any material, substantial variation of fundamental electrical properties with reduced size will be observed when the electronic energy level spacing exceeds the temperature [10]. When the size of crystal is lower than the mean path of carriers in bulk solid (usually higher than 200 nm), the electron mean free path may be affected by the size of crystal [11].

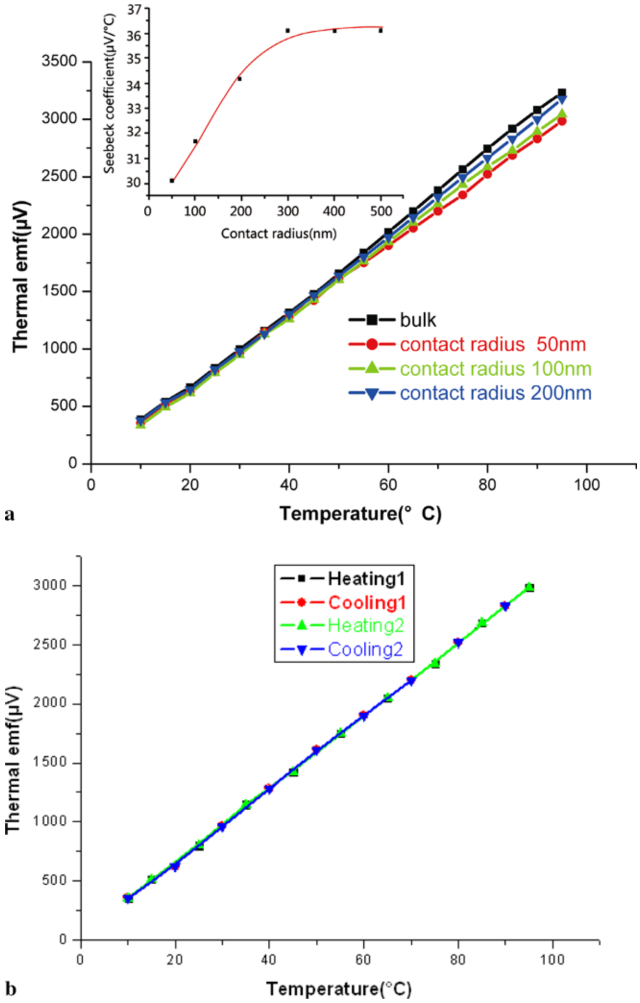

Fig. 4 (**a**) Characteristic curves of emf vs. temperature, for three different size thermocouples compared with a bulk thermocouple. Together with the Seebeck coefficient S as a function of the contact radius. (**b**) Heating and cooling curves showing the absence of hysteresis over two cycles

In our experiments, the size-dependent thermoelectric response should be ascribed to the variety of mean free path. The CuNi section is macroscopic and the nanoscaled effects result from the tip size. The emerging point of size effect is 300 nm, which approximates the critical size of mean free path of carriers. For the materials with size above 100 nm, the Fermi energy may be still constant. Due to the geometric refinement, the mean free path will become smaller than that in the macroscopic materials. Thus the Seebeck coefficient becomes smaller, and S decreases with the tip size turning smaller.

4 Conclusions

The thermocouple in tip-section structure may be used to probe the small heat fluxes in microcosmic conditions, even in a single cell. We fabricated the tip-section typed TC and the contact area of TC can be adjusted. The thermoelectric response of tip-section structured thermocouples showed size-dependent effects when the size is below 300 nm. Moreover, the output thermal emf versus temperature keeps nearly linear from 0 to 100°C like bulk behavior. We think the preliminary results will be valuable for the research of temperature measurement in single-cellular or sub-cellular scale.

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