Development of Nanoscale Thermocouple Probes for Local Thermal Measurements

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We developed thermocouple probes consisting of constantan and chromel segments with nanoscale sharpness. The ends of wires made of these alloys were polished utilizing a single step drop-off electrochemical procedure in a H3PO4 solution. The macroscopic shapes of the etched wires were designed to detect ultra-small heat inputs with high sensitivity after assembling a thermocouple. After electrochemical treatment, ultimately smooth, mirror-polished wire surfaces were observed. The etched wires were then assembled in a transmission electron microscope (TEM) to create a miniature thermocouple by using which we successfully detected a small temperature increase induced by focused TEM electron beam irradiation. Judging from high-resolution TEM imaging, a thermocouple with the tip-end of only ~5 nm in diameter was fabricated.

Keywords Electrochemical methods; Multi-probe method; Transmission electron microscopy; Constantan; Chromel

I. INTRODUCTION

Nowadays the preparation of sharpened probes, down to the nanoscale dimensions, becomes essential for many fundamental physical chemistry and application fields. Scanning tunneling microscopy (STM), one of the scanning probe microscopy techniques, is the most powerful method to observe single-molecules at nanoscale via utilizing atomically-sharp metal tips. For STM measurements, the tip quality, such as its geometry, shape and cleanliness, is the most important factor to achieve atomic resolution. Probe methods have also been used in a field of micromachining [1] and electronics [2]. Sharp tips are also needed for tip-enhanced Raman spectroscopy (TERS) to characterize biomolecules [3].

Numerous studies have been conducted to design the right tip preparation technique. For instance, electrochemical etching of W wires has been used because of its simplicity and convenience. Several reproducible and reliable methods have been reported to prepare W tips having diameters of ~5 nm or less [4, 5]. To enhance Raman scattering efficiency, gold [6] or silver [7] tips have conventionally been used, which are prepared by utilizing the regarded electrochemical procedure.

Here we note that almost all the pre-reported high quality tip materials have been made of simple substances. In the case of chemical treatment of an alloy, complex chemical reactions often make tip quality not good enough due to a significant difference in chemical nature of various elements. For example, a Pt-Ir alloy, a commonly used material in the field of STM, as well as tungsten, are sharpened by using mechanical cutting method, rather than electrochemical
treatment. If it would be possible to prepare ultimately sharp alloy tips via electrochemical processing, it may result in a new and effective sensing technology that may shed a new light onto nanomaterial properties and functions. Especially, these days, nanoscale thermometry becomes extremely important from a viewpoint of designing energy-harvesting devices, such as heat sink materials and nanostructured thermoelectric devices. At present, thermal characterization is usually conducted by employing microelectromechanical system (MEMS) devices which use a platinum resistance thermometer [8]. However, it is not possible to evaluate nanomaterials having inhomogeneous structures, such as heat sink nanocomposites, because MEMS can only evaluate integrated thermal properties over the electrodes /thermosensors. It is envisaged that a movable nanoscale thermosensor is desirable to measure local thermal properties of an inhomogeneous structure.

For instance, Gao et al. have reported on the formation of a nanothermometer by using a liquid gallium-filled carbon nanotube with a diameter ranging from 48 nm to 145 nm [9]. This study paves the way toward development of a movable local heat sensor placed at the desirable position. However, there have been many technical problems for the practical implementation of such nanothermometers because of necessity of preliminary calibration.

In recent years, we have developed an original method to analyze local heat pathways within inhomogeneous nano-materials, named by us as “scanning thermal analytical microscopy” (STAM) [10]. STAM is an original technique based on combination of a scanning heat input [from a focused electron beam under scanning transmission electron microscopy mode (STEM)] with the piezo-driven nano-thermocouples. By monitoring the temperature detected at the thermocouple position, while changing the heat input position, two-dimensional heat maps are obtained. In order to get clear STAM image, high temperature sensitivity is essential, which depends not only on the power of heat input, but also on the thermocouple quality.

In this study, we demonstrate the ultimate fabrication of an ultra-sharp nanoscale thermocouple for STAM measurements. For the preparation of the sharpened alloy tips we developed a single-step drop-off electrochemical etching procedure. The tip-end shapes are designed for particular thermal analysis. The technique is easily applicable to other alloy materials thus nicely contributing to the field of nanoscale probe sensing applications.

II. EXPERIMENTAL METHODS

A. Selection of tip materials for nanoscale thermal sensing

We chose a type E thermocouple (chromel-constantan) in this study judging from the following reasons.

First, we considered an experimental setup of STAM. STAM was conducted in a STEM-compatible instrument because the tips were able to be assembled under precise position control using real-time transmission electron microscopy (TEM) observation. At present, we assembled nanoprobes in an area between lower and upper pole pieces of an objective lens of STEM. Because this area was subjected to a magnetic field of 2 T, the magnetic materials, which disturbed STEM observation, were not suitable. This was the reason why standard K-type thermocouple materials were not suitable for our experiments, i.e., alumel possesses some magnetism. We then investigated the characteristics of many thermocouple types and finally concluded that the E-type thermocouple, a combination of constantan and chromel, had a desired nonmagnetic character and possessed the high Seebeck coefficient.

Next, solubility in chemical solution was investigated. One of the most difficult factors for making etched surface smooth under electrochemical treatment of an alloy is the difference in chemical nature of each element. This would cause unexpected inhomogeneity during an etching process. Constantan and chromel are the alloys of Cu-Ni and Ni-Cr, respectively. They consist of 3d transition metals, which easily dissolve in most of acid solutions.

Formation of mechanically strong and stable contact between wires is also an important factor for the further usage. In such a case, the simple mechanical contact of two probes could be not good enough, because the thermoelectromotive force often fluctuates due to instability of contact thermal and electric resistances. To solve this problem the wires was contacted and then bonded by using a direct current heating method employing a source measure unit, which was similar to welding, as shown below. In order to investigate whether the wires made a strong contact, we tried a resistance spot welding between bulk constantan and chromel wires, and found that they indeed

![Figure 1: Schematics of electrochemical etching setup for constantan and chromel tips.](image-url)
were able to form a mechanically strong contact. Thus, the assembled thermocouple in TEM was expected to work stably during the temperature measurements.

B. Experimental apparatus for electrochemical etching

A schematic view of the experimental setup is shown in Figure 1. Constantan and chromel wires of 0.20 mm in diameter (Nilaco Corp.) were cleaned in ethanol by using an ultrasonic bath. Then, they were attached to a sample holder of a dip coater (AIDEN, DC4200) which also worked as a wire height controller. The wires were immersed in a droplet of 85% H₃PO₄ aqueous solution held by a gold loop. The initial immersed lengths were controlled to be ~7 mm. We did not use multi-step etching technique [2], which finishes polishing at a low current condition, because etching (case of Cu in phosphoric acid) at a low current condition makes the surface rough [11]. After that, a stainless steel saucer fixed onto a compact laboratory jack was lifted up to softly contact the bottom wire end. This contrivance was our original design which brought about many merits as follows. First, it prevented the wire from mechanical vibration caused by bubbling during etching. Because constantan and chromel were not mechanically strong like, e.g., tungsten, bubbling effect might be detrimental. In addition, the dropped part was able to be easily salvaged. The upper and the lower parts would have the same end size just after wire cutting. Thus, the production rate of probes became twice more effective.

Next we considered the effect of a post-etching. In the case of tungsten tip etching, it has been reported that post etching phenomenon during electrochemical etching causes tip end to become blunted [1]. Thus, we made a new circuit to cut an applied voltage after detecting sudden drop of etching current in order to avoid excess etching. It also enabled us to ensure that the mechanical and electrical contact between the wire and the saucer was good.

C. Electrochemical etching procedure

The etching conditions were controlled at the following manner. A direct current (DC) voltage of 5.0 V was applied between the tip and the loop using a DC power supply (Kikusui, PMC18-1A) under the constant voltage mode. We should note that the experimental conditions were valid for both constantan and chromel wires. Typically, we started with a ~20 mA etching current, and it took ~15 min to drop the bottom part of wire. Then, they were immediately salvaged and repeatedly rinsed with enough amount of deionized water. After that, the residual water around the ends of the probes was removed by N₂ gas blow-off. The produced probes were stored in a vacuum desiccator just before thermal analysis experiment.

D. Optical and TEM observations

We checked macroscopic shapes of etched tips by using a digital microscope with a universal zoom lens (Keyence, VHX-900 and VHX-Z100UR). We used a JEOL JEM-3100FEE (Omega Filter) field emission high-resolution TEM for further measurements.

A twin-probe scanning tunneling microscopy (STM)-TEM holder made by “Nanofactory Instruments AB” was used to assemble a nanoscale thermocouple in TEM. The microscope was operated at an acceleration voltage of 300 kV. A DC voltage/current source/monitor source meter (ADCMT, 6241A) was used to measure electrical resistance between the probes. Our experimental system was able to detect a thermo-electromotive force at < 1 μV noise level [12], corresponding to < 0.02 K in the temperature change calculated from a Seebeck coefficient of 61 μV. More details of STAM measurements are described elsewhere [10].

III. RESULTS AND DISCUSSION

A Optical microscope investigation

As described above, difference in etching rate for dissimilar metals is one of the serious problems, resulting in a rough alloy surface. The rough surfaces are easily identified optically (Figure A1 in Appendix) after etching with a H₂SO₄ based solution. When the etched surface exhibits a metallic luster, it is expected to be smooth. Thus, before TEM analysis, it is worth observing the metal surface with an optical microscope.

Figure 2: Optical images of (a) constantan and (b) chromel probes after electrochemical etching in a H₃PO₄ solution under an applied voltage of 5.0 V.
Figure 2(a, b) shows typical optical images of the sharpened constantan and chromel probes. We could obtain metallic luster surfaces for both constantan and chromel sections. Their shapes are quite similar with those of tungsten probes previously reported [2].

B TEM observation for building thermocouple assembly

Next we performed TEM observation and the thermocouple assembling. From the viewpoint of heat detection, the entire shapes of the resulted probes are quite important for further thermal analysis, especially in the case of a small heat input.

Figure 3(a, b) shows bright-field (BF) TEM images of typical tips having low- and large-end volume. In Figure 3(a) the narrow wire region continues over several hundred nanometers, whereas the tip shown in Figure 3(b) has a large volume, although its tip-end is sharp. If the narrow region is short, like for this tip, the thermocouple works as a heat sink rather than as a sensor; heat is easily dissipated, resulting in a small temperature rise at/around the wire contact. In other words, a large portion of heat is consumed to increase the internal energy of the tip ends. The small volume of the tip end leads to the small heat capacity, resulting in a quick temperature response. Now it takes only ~1 s to get a STAM signal at each point [10], being (in a temporal sense) comparable to other analytical microscopy methods based on TEM, such as energy dispersive X-ray spectroscopy mapping. However, an excessive length of the narrow wire region makes its mechanically weak. Intensive mechanical vibration is typical under moving the probes, this may result in the fatal crashes of wires or wire and sample contacts.

Figure 4(a, b) shows typical BF-TEM images of the etched ends of constantan and chromel wires. The tip-end diameters of constantan and chromel are estimated to be ~12 nm and ~7 nm, respectively.

After the TEM observation of each probe, we carefully put the probes in contact. After that, a small current (~100 nA) was applied between probes until the wire connection started to show an Ohmic behavior. In our present setup, the joint typically shows the resistance of the order of ~1 kΩ or less [10]. We assume that this resistance increase compared with that of bulk wires may be due to the macroscopic shapes of wires, rather than to point-like contact resistance at the interface. We found that once the thermocouple was assembled, it was hard to separate the segments non-destructively. This ensures that the assembled probes can move together, although we cannot move two piezo-driven systems at the same time. It also means that the probes should be disposed after each experiment, however, this issue is solved by a reproducible production of numerous tips.

Figure 4(c) is a high-resolution TEM image after probes assembling, as referred to our previous report [10]. The tip diameter of ~5 nm has been achieved. This is smaller than the Ga-filled carbon nanotube thermometer [9] by one order of magnitude.

The nanothermocouple have been designed for STAM measurements. Figure 5(a) shows a schematic view of STAM. A square column shape sample consists of two fillers 1 and 2, and they are distinguished by (thermal) boundary interface at section B−C. This specimen can be fabricated by using a focused ion beam. The fabricated specimen is supported on a metal base through the pasted thermal insulator resin such as epoxy. Constantan and chromel nanoprobes are assembled in TEM and then attached to the other end (position M). After that, a focused electron beam
is irradiated at a desirable sample position can generate local heat through a relaxation of a plasmon excitation. After reaching a thermally steady-state by a continuous electron beam irradiation, an electromotive force can be monitored by a thermocouple. Please note that input heat can mainly pass through the specimen in the direction to the thermocouple because the supporting metallic base is thermally insulated by epoxy resin. It is also important that temperature at the thermocouple (position M) is different from that of sample due to the thermal contact resistance between the thermocouple and the sample. By repeating this procedure while changing the heating position [from position A to D in Figure 5(a)], we can get a thermoelectromotive force response in terms of heating position, as shown in the lower part of Figure 5(a). The signal behavior is explained on the basis of Fourier’s law which is expressed as the following formula.

\[ Q = -k \frac{dT}{dx} \]

Here \( Q \), \( k \), and \( \frac{dT}{dx} \) are a heat flux, a thermal conductivity, and a temperature gradient, respectively. At a thermally steady-state, \( Q \) does not depend on heating position where consist of the same material, such as intervals of A–B and C–D. Under this experimental condition, the temperature gradient is in linear relationship with an inverse of the thermal conductivity. Here temperature is also proportional to a thermoelectromotive force. Therefore, a thermoelectromotive force gradient is proportional to an inverse of the thermal conductivity. A large gradient corresponds to a small thermal conductivity, i.e., a large thermal resistance. When the two fillers have the same electronic structures, \( Q \) and \( k \) are also considered to be the same, resulting the uniform signal gradient [red lines in Figure 5(a)]. The signal gradient between the two fillers, which can be also calculated from the differences in signal and distance as shown in the blue line in Figure 5(a), corresponding to the thermal interface resistance. By assuming the thermal conductivity of fillers to the reference value, the thermal interface resistance can be calculated from a ratio of these two signal gradients. Actually, we have successfully estimated the thermal interface resistance between alumina fillers in the previous study [12]. Here it is not needed to know information on actual sample temperature and thermal interface resistance between a sample and a thermocouple, which are much difficult to evaluate. It is one of the most important features of our developed STAM method. Temperature resolution of our setup is < 0.02 K judging from a noise level of thermoelectromotive force signal (< 1 μV) and a bulk Seebeck coefficient of constantan-chromel thermocouple (~61 μV K\(^{-1}\)). The amount of input heat is calculated to be \( 8.4 \times 10^{-7} \) W, depending on the physical properties of samples and the electron beam condition. The detailed of the measurements and analyses was described elsewhere [10, 12]. Thus, we have successfully detected temperature change induced by such a small heat input condition.

IV. CONCLUSION

We demonstrated the preparation of nanoscale thermocouples consisting of constantan and chromel alloy segments. We successfully fabricated extremely sharp tips under the common etching conditions. The etched wires were observed in TEM, revealing the tip sizes of only ~12 nm and ~7 nm in diameters for constantan and chromel probes, respectively. Consequently, the assembled thermocouple of ~5 nm in diameter was prepared. Our method for easy preparation of sharpened nanoscaled probes may be applicable to other alloy materials and should be useful in the field of both fundamental research and applications.
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Appendix

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Figure A1: Optical image of constantan probe having a rough surface.

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