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SCANNING PROBE ELECTRICAL CONDUCTIVITY MEASUREMENTS USING SUBMICRO-ELECTRODES FABRICATED BY NONLITHOGRAPHIC TECHNIQUES

By

Akiko Kubota

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Electrical and Computer Engineering

2003

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ABSTRACT

SCANNING PROBE ELECTRICAL CONDUCTIVITY MEASUREMENTS USING SUBMICRO-ELECTRODES FABRICATED BY NONLITHOGRAPHIC TECHNIQUES

By

Akiko Kubota

The measurement of electrical conductivity of a substance at extremely localized areas can be realized through utilization of micron-scale probes fabricated using the Sutter® P-2000 CO₂ laser micropipette puller. These probes are composed of a glass tube containing a metal wire. Using the micropipette puller, the glass/metal combination is then pulled in two steps. The first step is to pull down the glass tube around the wire and the second step is a final pull to achieve the tip dimension of micron or sub-micron diameters. By manipulating the parameters on the micropipette puller, which among others include the heat of the laser and the force of the pull, this type of "nano-probe" can be constructed. The goal of this thesis was both the formulations of a fabrication process and the subsequent application of the nano-probe. After the nano-probe was successfully fabricated, it was employed in a scanning probe electrical conductivity measurement system. This system is very useful for obtaining electrical conductivity variations over an entire sample (up to 1" x 1") and for investigating nonuniformities (in the form of doping variations, surface cracking, etc.) that might exist in a sample. The design and testing of this system will be presented, along with data from several samples.

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1. INTRODUCTION

1.1 Thermoelectric effect

Transport measurements are essential to the development of novel electronic materials and electronic devices. In semiconductor materials, these measurements can be sensitive to parts per million concentrations of dopants. They further give us insight into the development of accurate models for materials and their structures which can then be used for engineering new devices. Of particular interest to our laboratory has been new narrow bandgap materials which exhibit promising thermoelectric transport properties.

A thermoelectric (TE) cooler, sometimes called a thermoelectric module or Peltier cooler, is a semiconductor-based electronic component that functions as a heat pump. Solid State thermoelectric coolers have been studied since the discovery of the Peltier effect in 1834, however, the devices became practical only recently with the development of more efficient semiconductor thermocouple materials [1]. Although thermoelectric coolers are not the solution for every cooling system, they are suited to wide variety of applications. Their advantages include small size, low cost, low weight, wide operating temperature range, or precise temperature control, and high reliability. Traditional applications of TE coolers have included temperature control of infrared detectors, cooling of electronic components (IC's), and small (personal) coolers/refrigerators. It is also possible to utilize thermoelectric modules for power generation when a temperature gradient is established across the module. This has found applications in satellite power supplies, remote site power generations, and waste heat power recovery.

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The most common thermoelectric material is bismuth telluride, (Bi_2Te_3) , which often alloyed with selenium and antimony, is the highest efficiency thermoelectric material known for near room temperature applications.

The typical thermoelectric module consists of two thin ceramic plates with an array of p and n doped bismuth-telluride semiconductor materials sandwiched between them. The ceramic materials on both sides of the thermoelectric module provide optimization of the electrical insulation and thermal conduction with high mechanical strength. One p-type leg and one n-type leg make up a couple, as shown in Figure 1.1.







Figure 1.1 Thermoelectric couple to form a module

The thermoelectric couple is electrically connected with metallic strips to form a module. Multicouple modules can be fabricated for larger heat pumping capabilities by connecting the couples electrically in series and thermally in parallel. A thermoelectric module can contain one to several hundred couples or more. Modules can be mounted in parallel to increase the heat transfer effect or can be stacked in multistage cascades to achieve high differential temperatures.

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Once a small DC voltage is applied across the couple in the configuration shown in Figure 1.2, the majority carriers of each leg will be transferring from the top to the bottom of a module. In the case of n-type leg, electrons transfer from the top of the module to the bottom of the module. These electrons not only carry charge as the flow, but they also carry heat. This transfer of heat is the result of electrons absorbing vibration energy from the surrounding crystal through scattering events. Since the average motion of the electrons is from the top to the bottom, the thermal energy they carry to their next scattering event also flows from the top to the bottom in this configuration.



Figure 1.2 Principle of thermoelectric cooling

The e p-type materi determined thermoelectri operational t contains thes Z (with units where S is th of the semi therefore the of merit car thermal cond majority carr cold to hot s ^{a higher} valu R. and thus desired to he the maximum type materia The efficiency of this device is dependent on a combined effect of the *n*-type and *p*-type materials used in making the module. The quality of a particular materials can be determined through the materials properties of absolute Seebeck coefficient (or thermoelectric power), electrical conductivity, and thermal conductivity over the operational temperature range between the cold and hot sides [2]. The expression that contains these material parameters is referred to as the figure-of-merit, and is denoted by Z (with units of reciprocal Kelvin)

$$Z = \frac{S^2 \sigma}{\kappa} \qquad (1.1)$$

where S is thermopower, σ is electrical conductivity, and κ is thermal conductivity. Each of the semiconductor material properties varies as a function of temperature, and therefore the figure-of-merit for each material is also temperature dependent. The figure of merit can be improved by increasing the electrical conductivity and decreasing the thermal conductivity. By having higher value of electrical conductivity, it ensures more majority carrier to transport from the top to bottom of the module, or pump heat from the cold to hot side. In other words, a higher value of mobility, μ , could also be the cause of a higher value of electrical conductivity, lower values are desired to help insulate between large temperature gradients. Also it can be shown that the maximum temperature differential that can be achieved by a single pair of *n*- and *p*type materials is directly proportional to the "temperature averaged" figure-of-merit of

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each semiconductor material. Therefore, maximizing the figure-of-merit is the major objective in the selection and optimization of thermoelectric materials.

1.1.1 Research objective

At Michigan State University, members of the Electrical and Computer Engineering Department, the Chemistry Department, and the Physics and Astronomy Department are collaborating through research on new thermoelectric materials. The researchers from the Chemistry group are studying the fabrication of compound semiconductors, and have discovered many new materials. After a new sample is fabricated, researchers from the Electrical and Computer Engineering Department characterize the sample to determine the unit less figure of merit, *ZT*. As discussed in the previous section, *ZT* value includes the values of thermal conductivity, the electrical conductivity and the thermopower of the sample.

This thesis focuses on the development of scanning probes for electrical conductivity characterization of new electronic materials such as the thermoelectric compounds discussed above. The electrical conductivities of the compound semiconductors can be measured by a four-point probe method, which will be further discussed below. Because the sample often has dimensions of small single crystals with dimensions near [$10\mu m \times 50\mu m \times 1mm$], in order to measure the conductivities of such a small sample, voltage probes with submicron diameters have been developed. In the fabrication process of these probes, a laser-based micropipette puller P-2000 is used as a pulling devices. In this thesis, submicron probe fabrication procedures and scanning probe measurement data are presented and discussed.

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1.2 History

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1.2 History of micropipette puller

Micropipette fabrication devices, including micropipette puller and micropipette beveller were first produced by the Sutter Instrument company in order to develop and manufacture precision electromechanical devices that could be used to overcome technical barriers associated with electrophysiology experimental techniques [3]. The micropipette puller is capable of melting and pulling a glass (or quartz) tube down to submicron tip dimensions while maintaining the tubular shape, thus they have been used to produce some of the fundamental tools necessary to perform biological research at a cellular level. In addition, micropipettes pulled by a micropipette puller can be found in many of the major scientific research organizations in the world. Micropipette fabrication technology accelerated the pace of biomedical research and emerging analytical techniques that utilize submicron probes and pipettes. The tremendous growth in nanofabrication methods, optical research, and imaging techniques expanded market focus beyond the boundaries of the biological research sciences. Micropipettes are now being used in a broad range of applications including, but not limited to, optical probe manufacturing, semiconductor research, electronics manufacturing, clinical diagnostics, infertility treatment, atmospheric research, astronomical imaging, fusion research, and material analysis.

In order to fabricate electrodes for two point, or four point probe conductivity measurements, the model P-2000 micropipette puller was selected for the following reasons:

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• P-2000 laser based Micropipette / fiber puller

The P-2000 integrates a CO₂ laser-based heat source with the technology derived from the extensive experience with conventional pullers. This system offers capabilities unmatched by other pullers. While the P-2000 is suitable for working with most conventional glasses, its primary advantage is the ability to work with quartz glass (fused silica). Quartz offers superior material properties for a variety of research applications. It is stronger than other glasses and can facilitate penetration through tough tissues which would normally break conventional pipettes [4]. Quartz can operate at higher temperatures and has been found to yield lower noise probes. For this reason, quartz is the best material to use in fabricating the nano-electrode cantilever beam used to measure the electrical conductivity. A CO₂ laser was selected as the heat source for the P-2000 for several reasons:

- The nominal emission wavelength of the laser approximates the resonant frequency of the SiO₂ lattice in glass. Thus quartz and other conventional glasses can be melted when the appropriate laser power is supplied.
- Laser heat is clean and leaves no metal residue on the pipette as do conventional heating filaments.
- 3) Laser heat can be turned off instantly, leaving no residual filament heat.
- 4) The user can program the amount and distribution of heat supplied to the glass. The additional versatility of quartz for other research projects was the main reason for choosing the P-2000.

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2. THEORY

2.1 Four point probe conductivity measurement

Four-point measurements have played an important role in understanding the electrical properties of solid state bulk materials and films for many decades [5]. A typical four-point configuration is a linear array of four equidistance electrodes. It consists of two outer electrodes performing as source and drain, and the inner electrodes measuring the voltage difference [6]. The conductivity, the reciprocal of resistivity, can be derived from the voltage-to-current ratio, while compensating for geometrical effects related to the thickness, size, and shape of the sample. Because of the infinitesimal size of the tip dimension, compared to the whole sample dimension, the contact resistance created by the probe tip can be safely neglected over the total impedance of the sample.

For the wafer conductivity measurement, the four point probe is preferable over a two point probe because the contact resistances associated with the two point probe can not be easily measured [7]. With a two point probe method, the true sheet resistance can not be accurately separated from the measured resistance. Since very little contact and spreading resistance is associated with the voltage probes, one can obtain a fairly accurate calculation of the sheet resistance which is then used to calculate the resistivity.

2.1.1 Bulk sample

The resistivity measurements is made on the flat ends of the crystal by the four-point probe technique [8].

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Figure 2.1 Schematic of 4-point probe configuration in bulk crystal

The assumption made in this measurement is that, the metal tip is infinitesimal and samples are infinite in lateral dimension. For bulk sample where the sample thickness t >> s, the probe spacing, a spherical protrusion of current is emanated from the outer probe tips. The differential resistance is [9]:

$$\Delta R = \rho \left(\frac{dx}{A}\right) \qquad (2.1)$$

The differential resistance R is integrated between the inner probe tips, (where the voltage is measured):

$$R = \int_{x1}^{x2} \rho \frac{dx}{2\pi x^2} = \frac{\rho}{2\pi} \left(-\frac{1}{x} \right) \Big|_{x1}^{x2} = \frac{1}{2s} \frac{\rho}{2\pi} \quad (2.2)$$

where probe spacing is uniformly s. Thus the distances of x1 and x2 are, s and 2s respectively (Figure 2.1).

Since the surface area of the sphere is $4\pi r^2$, the hemisphere would be the half value of it, which is $2\pi r^2$, and dotted lined hemisphere under the bulk substrate represents the current flow. Thus the area integrated is $2\pi x^2$ where x is the radius of the sphere originated from the I+ probe tip. Due to the superposition of current at the outer two tips, R = V/2I. Thus the expression for bulk resistivity is:

$$\rho = 2\pi s \left(\frac{V}{I}\right) \quad (2.3)$$

In this case, the assumption is that the wafer is infinite in dimension, with respect to the probe spacing, however in the reality, wafers are not infinite in extent. Therefore the right hand side of the equation must be multiplied by a combination of correction factors.

2.1.2 Thin sheet or wafer

For a very thin layer (thickness t << s), the current is emanated from the outer probe tip in ring shape as seen in the figure 2.2.



Figure 2.2 Schematic of 4-point probe configuration in thin wafer.

Therefore the expression for the area $A = 2\pi xt$, where x is the radius of the circle and t is the thickness of the sample. So the area integrated is the periphery of the dotted cylindrical structure. The derivation is as follows:

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi xt} = \int_{x_1}^{2s} \frac{\rho}{2\pi t} \frac{dx}{x} = \frac{\rho}{2\pi t} \ln(x) \Big|_{x_1}^{2s} = \frac{\rho}{2\pi t} \ln 2 \quad (2.4)$$

Consequently, for R = V/2I, the sheet resistivity for a thin sheet is:

$$\rho = \frac{\pi t}{\ln 2} \left(\frac{V}{I} \right) \quad (2.5)$$

Here, it is noted that this expression is independent of the probe spacing s. In general, the sheet resistance $Rs (=\rho/t)$ can be expressed as:

$$Rs = k \left(\frac{V}{I}\right) \quad (2.6)$$

where V is the dc voltage across the voltage probes (in volts); I is the constant dc current passing through the current probes (in amperes), and the factor k is a correction factor or

also often called the geometric factor. In the case of an infinite thin sheet, k=4.53, which is $\pi/\ln 2$ from the derivation. However, the factor k will differ for non-ideal samples that have a finite dimension with respect to the probe spacing. The correction factors for a circular sample with a diameter [d], and a rectangular sample with the side parallel to the probe line as [a] and the side perpendicular to the probe line as [d] are given in Table 2.1 [10].



Table 2.1 Correction factor k for the measurement of sheet resistance

	Circle	Square	Rectangle		
d/a		a/d = 1	- (1)	- (-1	- / - > - /
<u>a/s</u>			a/d = 2	a/d = 3	a/d ≥ 4
1.0				0.9988	0.9994
1.25				1.2467	1.2248
1.5			1.4788	1.4893	1.4893
1.75			1.7196	1.7238	1.7238
2.0			1.9475	1.9475	1.9475
2.5			2.3532	2.3541	2.3541
3.0	2.2662	2.4575	2.7000	2.7005	2.7005
4.0	2.9289	3.1127	3.2246	3.2248	3.2248
5.0	3.3625	3.5098	3.5749	3.5750	3.5750
7.5	3.9273	4.0095	4.0361	4.0362	4.0362
10.0	4.1716	4.2209	4.2357	4.2357	4.2357
15.0	4.3646	4.3882	4.3947	4.3947	4.3947
20.0	4.4364	4.4516	4.4553	4.4553	4.4553
40.0	4.5076	4.5120	4.5129	4.5129	4.5129
8	4.5324	4.5324	4.5325	4.5325	4.5324

2.2 Composite material

The word "composite" means "consisting of two or more distinct parts" [11]. In the case of the probes fabricated by the micropipette puller, the composite consists of glass and metal. Thus a material having two or more distinct constituent materials or phases may be considered a composite material. Composite material has significantly different physical properties than do the constituent materials.

Composites consist of one or more discontinuous phases embedded in a **continuous** phase. The discontinuous phase is usually harder and stronger than the **continuous** phase and is called the reinforcement or reinforcing material, whereas the **continuous** phase is termed the matrix. In the probes described here, the glass tube acts as the matrix and is more plastic than the metal wire, which acts as the reinforcement. **Corn**posite materials can show improve mechanical properties such as strength, stiffness, toughness, and high-temperature performance. Here it is the glass metal composite material that allows the probes to be pulled down to small dimensions (a task that is very difficult using a metal wire alone).

After the micropipette puller drew the glass tube down around the wire, it is assumed that a perfect bonding exists between the fibers and the matrix so that no slippage can occur at the interface. Thus the probe is stretched at the same rate during the second pull as shown in Figure 2.3. Therefore, the strains experienced by the fiber, matrix, and composite are equal:

$$\varepsilon_{c} = \frac{\Delta l}{L}, \quad \varepsilon_{f} = \frac{\Delta l_{f}}{L}, \quad \varepsilon_{m} = \frac{\Delta l_{m}}{L} \quad (2.7)$$
 $\varepsilon = \varepsilon_{c} = \varepsilon_{f} = \varepsilon_{m} \quad (2.8)$

13



Figure 2.3 Strain

Also the force applied to the composite material can be separated into the forces applied to the fiber and to the matrix (Figure 2.4).

$$F_c = F_m + F_f \quad (2.9)$$



Figure 2.4 Total force including force acting on the matrix and on the fiber.

Th	ne elasticity form
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Fi	ber elasticity is:
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The elasticity formula is:

$$E = \frac{\sigma}{\varepsilon} \qquad (2.10)$$

where σ is the stress, which is simply the force divided by the area. This is applied to the **composite elasticity**, the matrix elasticity, and the fiber elasticity.

Composite elasticity is:

$$E_{c} = \frac{\sigma_{c}}{\varepsilon} = \frac{F_{c} / A_{c}}{\varepsilon}$$
(2.11)

Matrix elasticity is:

$$E_{m} = \frac{\sigma_{m}}{\varepsilon} = \frac{F_{m} / A_{m}}{\varepsilon}$$
(2.12)
$$\Rightarrow F_{m} = E_{m} A_{m} \varepsilon$$

Fiber elasticity is:

$$E_{f} = \frac{\sigma_{f}}{\varepsilon} = \frac{F_{f} / A_{f}}{\varepsilon}$$
(2.13)
$$\Rightarrow F_{f} = E_{f} A_{f} \varepsilon$$

Now the total force acting on matrix and fiber is:

$$F_c = F_m + F_f = (E_m A_m + E_f A_f)\varepsilon \quad (2.14)$$

Using (2.14) in (2.11) gives,

$$E_{c} = \frac{\left(E_{m}A_{m} + E_{f}A_{f}\right)\varepsilon/A_{c}}{\varepsilon} = \frac{\left(E_{m}A_{m} + E_{f}A_{f}\right)}{A_{c}} \qquad (2.15)$$

Now the areas of the composite, the matrix, and the fiber are (Figure 2.5):

$$A_{c} = \frac{\pi}{4} d_{m}^{2}$$
, $A_{m} = \frac{\pi}{4} \left(d_{m}^{2} - d_{f}^{2} \right)$, $A_{f} = \frac{\pi}{4} d_{f}^{2}$ (2.16)

Figure 2.

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Figure 2.5 Cross sectional area of the composite, the matrix, and the fiber.

Combining equation (2.15) and (2.16), yields the composite elasticity as:

$$E_{c} = \frac{E_{m} \left(d_{m}^{2} - d_{f}^{2} \right) + E_{f} d_{f}^{2}}{d_{m}^{2}}$$
(2.17)

This equation can be used to select a fiber dimension that will match the glass to yield a desired Young's modulus at the tip of the probe.

2.3 Force calculation on the circular cross-sectional cantilever beam

The submicron-electrode is a single-ended cantilever, which is designed to bend in only one direction. The probe is mounted on the xyz translation stage and cantilevered at an

angle of 30°. W

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Figure 2

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angle of 30°. When the xyz translation stage controls the vertical movement to make contact between the probe and the sample, a perpendicular load is applied at the end of the cantilever beam (Figure 2.6)



Figure 2.6 Cantilever beam and its axis orientation

The deflection displacement y is and its first derivative with respect to x equals the slope θ .

$$\frac{dy}{dx} = \theta \qquad (2.18)$$

Similarly the second derivative of deflection is equal to the reciprocal of radius of curvature ρ .

$$\frac{d^2 y}{dx^2} = \frac{1}{\rho} = \frac{M}{EI}$$
 (2.19)

M is the moment, E is the elasticity, and I is the inertia. In order to calculate the deflection, the moment of the cantilever is required.

$$M = Fx \qquad (2.20)$$

Here, F is the large (Figure 2.6).
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Here, F is the load to the cantilever beam and x is the location of the moment measured (Figure 2.6). Using (2.20) in (2.19) gives,

$$\frac{d^2 y}{dx^2} = \frac{Fx}{EI} \qquad (2.21)$$

with the boundary condition:

$$y(L) = 0$$
 (2.22)
 $\frac{dy}{dx}\Big|_{x=L} = 0$ (2.23)

There is zero deflection (2.22) and negligible angle of deflection (2.23) at the anchor.

Taking the first and second integral of differential equation (2.21), the solutions are

$$\frac{dy}{dx} = \frac{Fx^2}{2EI} + C_1 \qquad (2.22)$$
$$y = \frac{Fx^3}{6EI} + C_1 x + C_2 \qquad (2.23)$$

Using the boundary conditions C_1 and C_2 can be obtained as:

$$C_1 = -\frac{FL^2}{2EI}, \quad C_2 = \frac{FL^3}{3EI}$$
 (2.24)

By plugging these coefficients into equation (2.23):

$$y(x) = \frac{F}{6EI} x^{3} - \frac{FL^{2}}{2EI} x + \frac{FL^{3}}{3EI}$$
(2.25)

Maximum deflection occurs at x = 0. Thus, the maximum deflection of a cantilever is

given by [12]

$$y = \frac{FL^3}{3EI}$$
(2.18)

where y is the o the cantilever b the beam. In order of the moment is a moment of oriented along 2.6.)

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where y is the cantilever vertical displacement, F is the force applied, L is the length of the cantilever beam, E is the elasticity of the cantilever, and I is the moment of inertia of the beam.

In order to determine the moment of inertia I for a circular cross section, the axis of the moment of inertia is required. Since the load is applied along the y direction, there is a moment of inertia about the Xc axis (Figure 2.7). (Note: In Figure 2.6, the x axis is oriented along the beam length but, here in Figure 2.7, the x axis is the z axis of Figure 2.6.)



Figure 2.7 the moment of inertia of circular beam

The moment of inertia is the product of a differential area dA and the square of its distance from an axis [13]. A more precise name is second moment, because, in contrast to the first moment the second power of distance is involved instead of the first power. Thus, in order to determine the moment of inertia of a circular beam, the cross sectional area of its beam must be determined (Figure 2.7). Since the cross sectional area is circular instead of rectangular, the expression $r^2 dA$ is called the polar moment of inertia

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of the differential area with respect to origin. It might have been called the moment of inertia I_z with respect to the z axis. For the entire area of which dA is a representative element, the polar moment $J_o = \int r^2 dA$, where $r^2 = x^2 + y^2$. Hence

$$J_{o} = \int r^{2} dA = \int (x^{2} + y^{2}) dA = \int x^{2} dA + \int y^{2} dA = I_{y} + I_{x}$$
(2.19)

First select an area $dA = rd\theta dr$. Since the differential element is at distance r from the origin, the polar moment $dJ_o = \rho^2 dA$. For the circular area

$$J_{o} = \int dJ_{o} = \int r^{2} dA = \int_{0}^{2\pi} \left(\int_{0}^{r} r^{3} dr \right) d\theta$$
$$= \int_{0}^{2\pi} \left[\frac{r^{4}}{4} \right]_{0}^{r} d\theta = \frac{r^{4}}{4} \left[\theta \right]_{0}^{2\pi} = \frac{\pi r^{4}}{2}$$
(2.20)

It is evident that the moment of inertia with respect to any diameter equals the moment of inertia with respect to any other diameter. Thus, $I_x = I_y$ and:

$$J_0 = I_x + I_y = 2I_x \quad (2.21)$$

From this fact, the moment of inertia I_x with respect to any diameter is equal to one-half the polar moment of inertia, or $I_x = \frac{\pi r^4}{4}$. The above technique is easier than finding I_x directly as $\int y^2 dA$. Thus, the moment of inertia (I) for a circular beam is given by

$$I = \frac{\pi r^4}{4} \qquad (2.22)$$

Thus the maximum deflection of circular cantilever beam is:



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Figure 2.8 Slope and deflection for cantilever beam

By trigonometry,

$$y = (\tan \theta)L \quad (2.24)$$

Combining (2.23) and (2.24)

$$\tan\theta = \frac{4FL^2}{3E\pi r^4} \qquad (2.25)$$

In this way the deflection angle formula is derived, and the formula will be used to verify the probe mounting angle in chapter 6, Data and Analysis.

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3. MICROPIPETTE APPLICATIONS

Nowadays, many researchers apply micropipettes in various field, and applications of this can be found in numerous articles in scientific literature. Basically, the pulled micropipette can be sorted into two categories: an electrode with a metal wire inside a glass pipette or simply a glass pipette pulled without any filament. In the following subsection, the kinds of micropipettes application will be discussed.

3.1 Micropipettes with metal filaments

Various metals and types of glass can be used to make an electrode probe by the micropipette puller technique. Each material is carefully chosen in order to meet the criteria necessary for a specific research application.

3.1.1 Micropipette-based submicrometer thermocouple[14]

The measurements of spatially localized temperature changes are required in studies of many physical and biological processes and objects. To measure the rapid temperature change at the cellular and subcellular level, a thermocouple with submicron contact size and a response time of a few microseconds is required. G. Fish [14], from the Hebrew University of Jerusalem, demonstrated a fabrication process of micropipette-based submicrometer thermocouple. The submicron thermocouple consists of a micropipette containing a platinum core, and the unit is coated with gold to make a gold-platinum point thermocouple at the tip of the micropipette.

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Figure 3.1 Schematic presentation of the sensing area of the pipette thermocouple.

In order to obtain optimal parameters of a thermocouple, it is necessary to reduce the size of the sensor d, the thickness of the gold coating h_w , and the cone angle of the platinum core β (Figure 3.1). The reproducibility of the technique using a Sutter P-2000 laser pipette puller is approximately 90%. A platinum wire, 80 mm in diameter, was placed inside a borosilicate tube with outer and inner diameters of 1.2 and 0.3 mm, respectively. The pipette wire assembly was placed in a P-2000 pipette puller in which five parameters could be optimized: temperature of heating, the length of the segment heated, delay time between turning the heat on and the beginning of pulling, the velocity of the pull, and the strength of the pulling. To find the optimal combination of these parameters, they treat their sample, consisting of a glass tube containing a platinum wire, as a composite material (CM). In this material, the heated glass tube acts as a matrix which is more plastic than the platinum wire which acts as the frame. During the pulling

procedure, the uniform thinn: smaller dimen-First, t platinum wire further pulling Subseq in the formation shape of the parameters at l D_w over the ex and the platinu when the glass The sec The pipette tip like coatings w the required thi time of depositi ^{of the} microther

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procedure, the surrounding glass acts to stabilize the metal and thus results in a more uniform thinning of the metal core. Therefore, the metal core can be pulled down to a smaller dimension before breaking occurs.

First, the glass tubes were pulled to an inner diameter that was equal to the platinum wire diameter. At this point, the sample was heated for several seconds without further pulling to ensure a firm connection between the glass and the platinum.

Subsequently, the pulling was performed slowly, in four stages, and this resulted in the formation of two glass pipettes that were filled with platinum to the end. The shape of the cone and the outer diameter was determined by the pulling program parameters at both steps. At 0.2<A<0.4, where A is the ratio of platinum wire diameter D_w over the external diameter of the glass tube D_{gl} , it was possible to pull the glass tube and the platinum core to dimensions as small as 50 nm. The Pt electrode is clearly seen when the glass at the tip is etched back.

The second thermoelectrode was made as a vacuum-evaporated thin gold film. The pipette tip was facing the gold source. This geometry, succeeded in producing edgelike coatings with a maximal thickness of the gold layer near the tip. The coatings with the required thickness and electrical conductance were obtained by varying the rate and time of deposition. This improved the spatial resolution of thermocouple. The sensitivity of the microthermocouple produced was about 7 μ V/°C, which is slightly less than that of a bulk gold-platinum thermocouple.

3.1.2 Cantilever

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3.1.2 Cantilevered glass multiple-wire force-sensing thermal probes.[15]

With the further study on thermocouple, Dr. Dekhter[14] published the article on their modified thermocouple with force-sensor. A double platinum wire cantilevered glass probe was produced for scanned probe microthermal resistivity, and topographic measurements. For such a double-wire probe fabrication, borosilicate theta capillaries with an outer diameter of 1 mm were used. Platinum wires, 25 μ m in diameter, were inserted into each of the two channels of the capillary, and the combination was pulled in a Sutter P-2000 pipette puller to a small tip with a diameter of about 100 nm. In order to produce a sensitive element, the glass on the tip was removed by etching in HF, so that the two thin Pt wires were exposed to a length of about 3-10 μ m. The distance between the wires is 200-1000nm. To create a point of resistance, the two protruding wires were fused by heating the tip (Figure 3.2).



Figure 3.2 Overview of the fabrication of a double-wire thermal resistive probe.

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Near-field ^{scanning} probe r The resistance of the fused wires, 20-60 Ω , depends on the length and thickness of the protruding wires. The diameter of the fused wires is 100-200 nm. Subsequent to this operation, the straight tip is cantilevered about 150-200 μ m from the end. In order to produce a high refractive surface for the feedback control the cantilever of the probe was coated with gold. The cantilevered probe was then mounted on a special tip mount for placement in a Nanonic NSOM/AFM 100 confocal system scanned probe microscope. In this probe, a variation of 1°C in temperature corresponded to a variation of 0.1 Ω in the probe resistance. A constant current of about 4 mA was passed through the probe and this heated the sensitive resistive wire at the tip. The probe was brought into contact with the test sample and the heat flow passed into the sample surface. During scanning across the surface, the probe cooled faster in a region with higher thermal conductivity. The resistance of the probe was changed by this cooling and these variation were detected by the control system.

3.2 Micropipettes without metal filament

The glass micropipettes, pulled without any metal, can be used for controlled transport of materials such as liquid or gas. Also, they have been used as laser/optical wave-guides or as force sensors [1]. In addition, glass-pulled micropipettes are also applied to produce probe tips made from a single mode fiber for use in near-field scanning optical microscopy (NSOM).

3.2.1 The tip of Near-Field Scanning Optical Microscopy

Near-field Scanning Optical Microscopy, also known as NSOM or SNOM, is a scanning probe microscopy technique that allows optical imaging with spatial resolution

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beyond the diffraction limit. In this approach to optics [16], light is transmitted through a sub-wavelength aperture and the sample is placed within the near field at the distance from the aperture that is few times closer than the dimension of the wavelength of the light that is employed. Near-field (NF) is defined as the light that does not propagate through space but is localized on the surface of objects [17]. It is also called evanescent light or forbidden light. NF light contains more information, higher spatial frequencies, than far-field (FF) light which is the propagating normal light. Higher spatial frequencies exist at the sample surface; however, it decays exponentially within a distance less than the wavelength. By placing the sample within the NF of the aperture, the condition of aperture size $a < \lambda$ is satisfied, and a record of the optical interaction as a function of position can be generated. In other words, the sample will be resolved at the size of aperture.

There are various approaches being used to achieve the near-field light. In one method, the sample is illuminated with FF light. It can be completed either from the top surface (being imaged) or by the back illumination ATR (attenuated total reflection) geometry, which produces a near-field on the top surface of the transparent sample (Figure 3.3). The dark arrows represent the light path to sample (FF light), and the lighter arrows show the light from scattered near-field to detector.

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Figure 3.3 ATR illumination from the back of the transparent sample.

Introducing a sharp probe into the NF of the object scatters far-field (FF) that propagates and so can be detected by normal means such as a lens, CCD detector (Figure 3.4). In another method, a probe with a very small aperture is used to illuminate the object in the NF. A fiber optic terminates a FF light in a sub-wavelength aperture, and the probe tip is placed close to the object surface. The distance between probe tip and the sample is much less than one wavelength of FF light, so that the NF interacts with the sample surface. Again this information is converted to FF scattered light and thus it can be collected by the detector (Figure 3.4).





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Figure 3.4 Various methods of NSOM image capturing technique.

Recently, a new form of NSOM has been developed with the optical resolutions below 50 nm [18]. The device modified by the Dr. Lewis's research group in Hebrew University provide an integrated microscopic solution based on a near-field optical fiber probe that combines the possibility of near-field optics with atomic force microscopy. The conventional optical element is based on the introduction, by Hartoonian et al. [19], of glass tapering combined with metallic coating technology to near-field optics. The technique produced straight near-field optical elements, which are used in most of the applications of NSOM today. Nonetheless, the straight probes have limitation. To image the surface with a considerable degree of roughness, it is desirable for the tip to have a small cone angle over a length near its end which is larger than the surface corrugation height. In tip/cantilever combinations diamond shards have been used as tips that are hard, but they are not always sharp enough. In addition, such tips add considerable mass

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to the spring, thus lowering the resonance frequency. Microfabricated tip/cantilever combinations meet the second requirement, but the integrated tips are either short and fat, or prohibitively expensive.

Shalon et al.[20] presents a simple technique to reliably produce force probes from glass micropoipettes. Their modification of these micropipettes to sense surface forces not only provides a reliable and inexpensive solution to the difficulties mentioned above, but this modification is also of considerable importance for introducing a universal method of distance feedback that is essential in NSOM. The glass micropipettes used for NSOM can be bent near the tip to produce a structure that appeared to be readily adaptable to the most generally applicable and simplest methods of normal and lateral force sensing. The main drawback of such bent micropipettes for NSOM was that the sharp bend would prevent the light from reaching the subwavelength aperture at the tip. Thus, while the probe appeared interesting in its own right, it did not appear practical for NSOM. This problem has been resolved by the development of a new method of external excitation that produces a spot of light within the aperture at the tip, rather than transmitting a beam from a remote source through the entire length of the pipette [21]. This technique and the proposed combination are shown schematically in Figure 3.5.

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Figure 3.5 Dye-embedded sol gel ion-sensing cantilever micropipette [22].

A dye embedded plastic plug is formed inside the pipette tip and a laser beam is then directed head on to this tip generating a very intense fluorescence from the dye. With this method, besides receiving a very intense source of light, the excitation is uncoupled from the scanning probe and is not affected by the geometry of the pipette. This allows for a cantilevered pipette to be used for NSOM while simultaneously measuring the deflection of the cantilever due to normal and lateral surface forces with the standard methodologies used in force microscopy as depicted. The tips are fashioned from aluminum-silicate glass capillaries by a micropipette puller. After stretching by about 10 cm over an original length of 1 cm, the falling lower chuck activates a microswitch, which turns off

the heating. S lengths of mich the force sense the tip/surface bunsen flame viewed with a pipette aperture using the reflect cantilever. Sma glass cover sli cantilever. Wi has achieved of 3.2.2 Scanning Convent including micro much smaller resolution beyo scanning nanoli ^{photoresist} in th ^{end of the pull} ^{predetermined} p nanopipette. T the heating. Simultaneously, the capillary separates at its center, leaving two long, thin lengths of micropipettes, with a small hole at each end. These are the tips used to create the force sensors. To form the bend, which enables sensing of the force directed along the tip/surface axis, the micropipette tips are passed briefly over the hot air from a small bunsen flame which causes the end of the pipette to bend upwards. This process is viewed with a microscope, and it is challenging to get a good bend without closing the pipette aperture. Since the cantilevers were initially tested in a scanning force microscope using the reflection technique [23] for detection it was necessary to attach a mirror to the cantilever. Small pieces of mirror (50 μ m × 100 μ m × 100 μ m) were formed by coating a glass cover slip with aluminum and breaking it. These pieces were then glued to the cantilever. With a further study on NSOM, by the group from Dr. Lewis, this technology has achieved optical resolution below 50 nm, with the tip aperture as small as 50 nm.

3.2.2 Scanning nanolithography using a material-filled nanopipette

Conventional photolithography has been widely used in many applications including microelectronics and nanotechnology. However, due to the potential need for much smaller integrated electronics devices, nanolithographic methods for higher resolution beyond the present limit are studied. Mun-Heon Hong et.al. [24] presented a scanning nanolithography technique using a pulled micropipette which delivers liquid photoresist in the vicinity of the substrate through a nanometric aperture formed at the end of the pulled pipette [24]. In their scheme, the photoresist is deposited at the predetermined position on the substrate by ejecting it through the small aperture of the nanopipette. This approach has the following several advantages: (a) no spin coating of photoresist required, (b) no need of a mask, (c) no alignment of the mask and the substrate, (d) no need of UV light source, (e) no development process, (f) environment-friendly instrumentation in ambient conditions, and (g) simple and inexpensive.

The micropipette used in the experiment, pulled by a commercial pipette puller (P-2000, Sutter Instrum.Co.), is made of quartz with its inner (outer) diameter of 0.7 mm (1.0 mm). The pulled micropipettes can have hollow diameter ranging from a few tens of nanometer to a few hundred nanometers by adjusting the pulling parameters. A filament made of metal thread is installed inside the pipette so that its pulled tapered region can be mechanically strong. The filament is also designed to help the liquid photoresist wet the inner wall of the pipette so that the liquid can fill spontaneously inside the pipette. When the liquid, pushed by a syringe, is filled in a pipette without the filament, some trapped air remains inside. As the photoresist is pushed out, the effective mass of the pipette is changed, which results in a change of the resonance frequency of the pipette. Thus it becomes difficult to maintain the resonance frequency constant for shear-force feedback control. The xyz translation stage is controlled by shear-force detection. A shear-force detection scheme was developed by using two optical fibers placed in the vicinity of the pipette end (Figure 3.6): single-mode fibers for the focused light source as the incident laser, and two adjacent multi-mode fibers for differential optical detection of the diffracted light at the photodiode.



Figure 3.6 Schematic diagram of the photoresist-filled nanopipette controlled by shear force position detection [24].

The concept of shear force distance control is described further by A.D Muller [25]. Shear force distance control between a probe tip and a sample works in the following way. The whole tip is laterally excited by a dither piezo close to its resonance frequency. It behaves like an oscillator with small damping. While the tip approaches the sample surface, the shear force increases the damping. It follows a decreased resonance frequency and a decreased vibration amplitude. Both result in a decrease of the input signal for the feedback. The distance feedback maintains the percentage of amplitude decrease relative to the free oscillation constant. Alternatively, the phase shift between exciting and detected alternating signals can be utilized as an input signal for the feedback. The resonance shift and the amplitude decrease due to the weight and the damping of an evaporating drop of water over time. Their experimental configuration is based on the commercial optical detection system in the AuroraTM microscope head that was modified to carry micropipettes instead of optical fibers. The system provides an adjustable laser that can be directed towards the final end of the tip (apex) with an



incident angle of about 30°. During operation, the tip scatters the laser beam that is reflected on the sample surface, like shown in Figure 3.7.



Figure 3.7 Principle of the utilized optical shear force detection applied to the micropipette tip with a droplet near the apex [25].

In this way, the vibrating tip modulates the intensity of the reflected light with its oscillation frequency f_c . The detection system consists of a four quadrant photodiode. As tips, pulled micropipettes are mounted in the Aurora head and fasten by a screw. The pipettes were filled with distilled water that can be pumped and sucked in defined amounts. For the following experiments, there are no further requirements concerning the tip shape except that the liquid throughput has to be high enough to create a drop of water at its end. Typical inner apex diameters for this are of the order of 5-20 μ m. A water droplet is formed by pumping the liquid. Due to the sharp tip shape and the surface tension of water on glass, this droplet becomes stable some 10 μ m above the apex. Simultaneously, the laser beam points to a position above the water droplet so that the detected signal is not influenced by the drop of water. The sample has to be close enough to be able to reflect the laser beam. But sufficient distance from the apex is necessary for the existing water not to touch the sample surface. When the liquid pump is switched off, the drop size decreases continuously because the laser heats the micropipette and the

water droplet evaporates. This evaporation is so fast (some seconds for a 10 µm drop) that the frequency spectrum, which takes about 1 min to obtained with a lock-in amplifier, is difficult to correlate with a specific drop diameter. The resonance ω_i is given by $\omega_r = (\omega_o^2 - \Gamma^2/2)^{1/2}$, where ω_b is the resonance of the nondamped system (here the system without the drop). Therefore, the increase of the drop diameter is equal to an increase of mass *m* and reflectivity Γ of the drop as well as a decrease of resonance frequency ω_i and ω_i . In other words, resonance frequency is lower in the filled pipette, and intensity of the signal is larger in filled pipette due to the focusing effect on the scattered light on the drop (Figure 3.8).



Figure 3.8 Resonant frequency shift of the liquid-filled nanopipette (curve 2) with respect to that of the empty pipette (curve 1) [24].

Now, with the fundamental knowledge of shear-force control discussed above, the article written on nanolithography can be revisited. Even when the pipette-substrate distance is maintained constant, as the liquid is pushed out of the aperture (Figure 3.9 a), the liquid-substrate separation becomes small and consequently the shear-force signal is also decreased. The shear-force signal vanishes as in the case of the empty pipette. As

mentioned in the previous paragraph, intensity is larger in filled pipette because of the focusing effect on the scattering light on the drop. When the pipette retracts after the liquid is dropped, the signal returns to its original value (Figure 3.9 a). When the liquid flows continuously inside the pipette toward the aperture opening without discontinuity in mass distribution and if no liquid drop is formed at the end, the resonance frequency of the pipette does not change (Figure 3.9 b).



Figure 3.9 Two fabrication schemes: (a) point drawing and (b) line drawing [24].

However, if there is some trapped air moving inside, there exists a non-uniform mass distribution which results in the change of the resonance frequency depending on the position of the trapped air. This phenomenon can be used to monitor the smooth filling of the liquid in the entire pipette, by checking if the frequency changes while the liquid is pushed.

Figure 3.10 (a) shows the shear-force topography image of the three resist drops fabricated on the gold-sputtered substrate. The scanning image is obtained by using the same nanopipette as an NSOM probe. The separation between the dots is about 1 μ m and

the height of each drop is about 80 nm. The full width at half maximum linewidth of the dot is about 300 μ m, which is just the inner diameter of the nanopipette. Therefore, the rather large NSOM probe limits the resolution of the topographic image,[26] although the fabricated patterns can be much smaller depending on the drawing parameters such as liquid density, pressure, and approach/retract time.



Figure 3.10 Three photoresist dots of 300 nm size fabricated on the goldsputtered glass substrate. (a) Topographic image of the dots, and (b) height profile across the line in (a) [24].

4. FABRICATION AND APPLICATION OF MEMS MICRO CANTILEVER

In the conventional probe fabrication method, cleanroom facility was required for the probe fabrication process. The fabrication of a MEMS micro cantilever, requires many individual steps/processes as well a use of hazardous chemicals to etch the components. Although the micropipette puller was introduced to fabricate compatible or even better probes, it is still useful to review the fabrication procedure of MEMS micro cantilever and its application.

4.1 MEMS microfour-point probe

Conventional four-point probes are typically comprised of large, macroscopic tips of millimeter-scale spacing [27] or stationary, planar electrodes deposited on the sample using lithographic techniques [28]. The large contact forces exerted by macroscopic tips easily result in damage to sensitive surfaces. To avoid this problem, researchers from Dr. Boggild's lab have designed a new scanning micro four-point probe, which can be used non-destructively anywhere on a surface with a high spatial resolution [29]. The probe consists of four silicon oxide cantilevers on top of a flat silicon support, coated with a conducting electrode layer (25 nm Ti/ 100 nm Au). The cantilevers are 1.5 μ m thin, 7 μ m wide, and extend 60 μ m over the edge of the support. Due to their thinness, the cantilevers are flexible in the vertical direction and exert a contact force on the order of just 10⁻⁷ N for an electrode deflection of 1 μ m. The contact area is of the order 100 nm × 100 nm per electrode. Apart from reducing the surface damage, the advantage of using soft, flexible microcantilevers is that the cantilevers adapt more easily to height differences on the surface or misalignment of the probe. By measuring repeatedly over the same area and obtaining a constant result, they verify that the probe does not alter the electrical properties of the surface.

The probe is wire-bonded to gold film pads on the ceramic chip carrier, which is then mounted directly in a compact current source and preamplifier unit. A video microscope is located above the sample to monitor sample and probe during measurement. The probe is tilted 30° with respect to the sample, and aligned to the focal point of the microscope. The sample is mounted on a *xyz*-stage, which brings it into contact with the electrodes (Figure 4.1 (a)).



Figure 4.1 (a) Schematic of the experimental set up. (b) A scanning electron micrograph of the probe [29].

The resistance is determined from a linear fit to the V-I curve, where the bias current is being swept from -100 nA to 100 nA. The maximum bias voltage is limited to 0.5 V in order to avoid electrochemical reactions at the electrodes. To ensure consistent

mechanical conditions, they employ an optical force-feedback technique similar to that in atomic force microscopy. A laser beam is directed towards the cantilever, so that the reflection on the electrode can be detected in the microscope. When the cantilever touches the surface, the four reflection spots are dimmed due to the deflection of the cantilevers. By measuring the intensity of the reflection spots, the height differences of the surface are detected simultaneous with the electrical measurement.

4.1.1 Fabrication of micro four point conductivity probes

The micro-four-point probe is fabricated by conventional silicon processing techniques [30]. The process sequence is summarized in Figure 4.2. First a 1.0 μ m thick layer of SiO₂ is grown by wet oxidation on a 340 µm thick (100) silicon wafer (Figure 4.2 (a)). Then a 0.8 µm thick layer of photoresist (Hoechst AZ 5214E) is spun on top of the SiO₂ layer, and is exposed to UV light through a chromium mask defining the electrode pattern on the wafer front surface. The resist is then developed using the negative development process for AZ5214E. A thin chromium layer (750 Å) is deposited and lifted off, serving as a mask for the subsequent reactive ion etching (RIE) process in CHF₃ plasma (Figure 4.2 (b)). The oxide is RIE-etched to form four microcantilevers. After the chromium is removed a thin (1000 Å) layer of silicon nitride is then deposited on both sides of the wafer as a mask for silicon etching (Figure 4.2 (c)). A photoresist layer is deposited on the wafer backside and is patterned to define the probe support chips. The substrate is etched in a KOH solution at 80 °C until the wafer has been completely etched through from the rear side (Figure 4.2 (d)). At this point, the silicon

oxide microcantilevers are suspended over the edge of the support chip, but still covered with a thin nitride membrane. The silicon nitride membrane is removed by RIE in a mixture of SF₆ and O₂. A low-stress nitride reduces the risk of damaging the microcantilevers during the etching of the suspended membrane. Using an isotropic RIE silicon etching process with SF₆, the electrodes are undercut (Figure 4.2(e)). Because of the undercutting of the oxide structures, the metallization is maskless. The undercut structure allows silicon support chips to be coated individually or on a full wafer basis. For measurements in ambient condition a typical layer sequence of 250 Å Ti / 1000 Å Au is chosen, due to the excellent contact properties and low stress, resulting in a negligible bending of the electrodes.



Figure 4.2 The major steps in the microfabrication process.

4.2 Scanning nano four-probes or nano tweezer

In this manner, four soft and flexible metallized SiO₂ microcantilevers, with electrode spacings down to 1.5 μ m, were fabricated. To reduce the gap even further, an electron-beam induced deposition, which is a constructive three-dimensional nanolithography technique has been used [31]. By focusing the electron beam of a scanning electron microscope on the ends of the microcantilevers, hydrocarbon molecules present in small concentration near the beam spot are cracked. This leads to the formation of a narrow rod of carbon residues, growing in the direction of the electron beam. Lengths of several microns are easily obtained by continuation of the process, and such tip have successfully been used for high aspect ratio atomic force microscopy tips [32], nanoparticle manipulation [33], and nanolithography [34,35].

To avoid charging of the oxide cantilevers by the electron beam, and thus a poor growth rate and tip quality, the microcantilevers are coated with a thin metallic layer (100 Å Ti / 800 Å Au) prior to tip deposition (where 250 Å Ti / 1000 Å Au was deposited for the microcantilevers). By keeping the electrodes at the ground potential of the scanning electron microscope (SEM), a drain for the electron beam is provided.

The nanotips are grown at an acceleration voltage of 10 kV and beam current of 3-6 pA in a JEOL 6340F field emission microscope operating at a base pressure of 10⁻⁸ Torr. Higher beam current reduces the growth rate, possibly due to the increased charging and thus beam deflection. A growth rate of 250 nm/min was obtained by this technique. The beam current is comparable to the 1.9 pA found to be optimal by Wendel et al. [34] in terms of growth rate and resulting sharpness of the tips. To obtain fast and reproducible results, it is crucial to carefully adjust the focus and to correct for astigmatism of the electron beam. The carbon tip resulting from this deposition technique is mechanically strong and durable, as demonstrated in earlier works. It has been suggested that the tip material is diamond-like, without being brittle, which would explain the exceptional durability. By tilting the microprobe with respect to the beam, it is possible to control the shape of the nanotips as shown in Figure 4.3.



Figure 4.3 (a) Schematic of the nanotip deposited in a plane perpendicular to the plane of the microcantilevers. (b) SEM image of micfrofour-point probe. (c) SEM image of nanotwo probe with 200 nm spacing. (d) Close up of 200 nm gap twoprobe. (e) SEM image of nanofour point probe with an average spacing of 330 nm [31].

In order to make the nanotips conducting they are metallized a second time with 100 Å Ti / 600 Å Au. Such cantilevers are used for not only scanning nano multiprobes but also nano tweezers. For lifting and manipulating of free-hanging or floating structures such as nanowires it is necessary to use opposing forces to seize and hold efficiently. Kim and Lieber [36] reported the first nanoscale tweezers in operation, where two carbon nanotubes, attached to metal electrodes on opposing sides of a micron thick glass needle, were used to manipulate nanoscale clusters and wires. The tweezers were closed electrostatically using a voltage difference between the nanotubes. There are, however, situations where a large field across the object to be manipulated or measured is not desired, such as biological systems and organic molecules. Even if the grabbed object is electrically insulating, the strong fields near the object can induce structural changes. charging and other unwanted side effects. To address this problem, the nano tweezers have been further modified to include a set of independent electrodes used for opening and closing the tweezers. As shown in the SEM micrograph in Figure 4.3 (a), the electron beam was focused at the ends of the cantilevers at a tilt angle of 45°. After 10-30 s, the instrument was switched to scanning mode, to reposition the beam target and thereby compensate for drift. Here, an important consideration during the fabrication process is that scanning at a high magnification will inevitably deposit a thin carbon film over the entire image field. By alternatively depositing and viewing, the beam could be targeted exactly at the tip of the rod. The length increase gave a measure of the growth rate, which in their case was initially 400 nm min⁻¹, but decreased to 200 nm min⁻¹ as the tip length increased. The second tip can be deposited at an angle of 90° with respect to the first (Figure 4.4 (b)). By a continuation of this procedure, with smaller and smaller exposure times, the gap size can eventually be brought down to about 100 nm. To finalize the gap, parallel secondary tip are deposited at the ends of the converging tips. This secondary parallel tips are deposited by short ($20 \sim 100$ s) depositions to facilitate holding of elongated objects such as nanowires. By continually monitoring the growth rate, and estimating the deposition times, the two tips can be fine-tuned to within 10 nm. In Figure 4.4(c), two such secondary tips are shown. This unique feature makes it possible to shape the tweezer to provide the best possible manipulation properties for a given application.



Figure 4.4 The nanofabrication process.

The nanotweezer is opened by applying a potential difference between the inner and the outer electrodes while maintaining a potential difference between the inner electrodes near zero. A small bias voltage can be used for measuring the grabbed object (Figure 4.5). In other words, the outer cantilevers are used as actuating electrodes, and a moderate voltage of around 10 V can open the gap without biasing the inner tweezer arms

with respect to each other. Thus, this results in avoiding electrical damage to the held object.



Figure 4.5 The circuit set up of nanotweezer.

5. MATERIALS AND METHODS

5.1 Electrode fabricated by micropipette puller

The measurement of electrical conductivity of a substance at extremely localized areas can be realized through utilization of micron-scale probes fabricated using the Sutter[®] P-2000 CO₂ laser micropipette puller. The probes are produced in two steps. First, a metal wire is inserted into a glass capillary tube. Using the micropipette puller, the glass/metal combination is then pulled down to micron or sub-micron diameters. By manipulating the parameters on the micropipette puller, which among others include the heat of the laser and the force of the pull, this type of "micro-probe" can be achieved. The goal of this section is to discover a reliable process that will create these micro-probes with high repeatability and consistency. This relatively simple technique for the fabrication of such cantilever probes can be extended to other sensing applications such as temperature measurements through additional coating steps.

5.1.1 Material selection

The critical element in drawing glass with a metal core is to get both the glass and metal to draw at the same time. In general this requires glass and metal with similar melting temperatures, and close contact between the glass and metal at least in the final draw.

In the best case (ideally), close contact is a complete metal core with no air gap between the metal and the glass. This insures the best heat transfer from the glass to the metal, and it also mechanically couples the metal to the glass. If a fine wire is simply placed inside a capillary with a much larger inner diameter, the metal will not be adequately connected to the glass mechanically, nor for purposes of heat transfer. In such a case, the glass first must be drawn down until it tightly surrounds the metal wire, so it forms one unit of glass and metal composite material. Then, in subsequent steps, the glass-metal composite can be drawn down together.

The glass and metal used in combination must have appropriate melting points. Through our experiments we have found that it appears the metal core should have a slightly lower melting point than the surrounding glass. Heat is applied at the outside surface of the glass and must conduct through the glass to reach the metal. Since the metal is heated by the surrounding glass, it follows that the metal must be slightly cooler than the glass. The metal has higher thermal conductivity than glass, so that the heat reaching the metal core will be conducted away toward the cool unheated ends of the metal wire more rapidly than in the surrounding glass. As the result, the metal doesn't get as hot as the glass during the heating phase. Thus, in theory, it is ideal that the metal has slightly lower melting temperature than the glass softening temperature. This insures metal and glass to fuse strongly and draw the composite further without any discontinuity. If the metal has higher melting point than glass, the metal never melts and the metal is more likely to break without any tapering (Figure 5.1). It is possible to utilize the higher melting point metal, if the glass can withstand temperatures in excess of its softening temperature. On the other hand, if the metal has far less melting point than the glass, the metal boils and forms bubbles in the glass tube (Figure 5.2). Thus the metal core would be discontinuous.

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Figure 5.1 The metal breaking at the tip



Figure 5.2 The metal boiling in the tube

Therefore, each metal melting temperature and glass working temperature is carefully checked in order to find the matched glass and metal combination (Table 5.1 and 5.2) [37].

Metal Type	Elasticity (E)	Melting temperature
Copper	110 GPa	1083 °C
Nickel	270 GPA	1455 °C
Platinum	171 GPa	1770 °C
Constantan	162 GPa	1300 °C
Gold	77.2 Gpa	1064 °C

Table 5.1 Metal physical properties.

Glass Type	Elasticity (E)	Softening temperature
Borosilicate glass	64 GPa	800 °C
Quartz glass	70 Gpa	1730 °C
Aluminosilicate glass	-	950 °C

Table 5.2 Glass physical properties.

Comparing the two tables above, it can be seen that the closest match between these metals and glasses is platinum and quartz. Although the melting temperature of platinum is a bit higher than that of quartz, this is still the best match because a full melt is not required to pull the metal; a partial melt will suffice, in addition the quartz can exceed 1730 °C to achieve a "softer" condition while pulling.

In Figure 5.3, the quart glass (o.d.=1.0mm, i.d.=0.3mm) and a platinum wire (diameter= 80μ m) were selected as the probe materials.



Figure 5.3 The pulled micropipette with platinum filament inside

After the final pull, the tip tapered and the wire decreased in diameter to $20 \ \mu m$. This result would suggest that it is best for the metal and glass to have similar melting point temperatures. It has been shown [38], however, that materials selected from largely

different melting point temperatures can also be used to draw the composite to make a probe. As written in the article, a platinum wire with 80 µm diameter and a borosilicate tube with outer and inner diameters of 1.2 and 0.3 mm, respectively, are used as probe materials. This would seem to run contrary to the argument stated mentioned above, since platinum has much higher melting point (1770 °C) than borosilicate glass softening point (800 °C), however, the properties of the composite for beyond the melting point for the glass were not discussed. This selection shows the melting point temperatures of metal and glass are not the only property for selecting materials. In order to stretch the wire and glass together, mechanical properties of the wire must also be considered. If the wire is soft, it stretches easily even without reaching full melt. Gold, with a hardness value of 25 Vickers, is a very soft metal. Platinum is next with a value of 40 Vickers. Silver and aluminum are also very soft metals but were not utilized with in this study. Thus in the case of the platinum wire in the borosilicate glass, it is considered that even though the melting point of platinum is higher than the borosilicate glass softening point, platinum is soft enough to get pulled down in the borosilicate glass tube without reaching full melt. It is also possible that the temperature exceeds the softening point of the borosilicate glass, but does not reach the boiling point of the glass.

The compliance of gold is vital in pulling the wire down in the pipette and achieving continuity to the very tip. Thus gold wire ($d=50\mu$ m) and borosilicate glass tube (i.d.=0.5mm, o.d.=1mm) were selected as the electrode probe for electrical conductivity measurements.

Selecting the dimensions of the glass tube and wire is also important for successful pulling. In addition, five parameters are programmed and optimized for each pair of tube/metal materials and dimensions by iterative testing. In the next section, those variables are discussed.

5.1.2 Laser Specification and Variables

The P-2000 contains a 20W Class IV CO₂ laser with a 3.5 mm diameter beam (spot size = 1.75 mm), and a 4 milliradian divergence.

The optimized structures of micropipettes with wires inside are determined by the parameter values that are programmed on the P-2000 by the user. There are 100 separate programs that can be saved for future use. Each of those programs consists of one or more cycles. A cycle consists of five programmable parameters; heat, filament, velocity, delay and pull. Those five parameters have some specific range of number to program in respectively (Table 5.3) [39].

Table 5.3 Five programmable parameters on P-2000	
Parameters	Range
Heat	0 to 999
Filament	0 to 15
Velocity	0 to 255
Pull	0 to 255
Delay	0 to 255

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The first parameter is heat which determines the power of the carbon dioxide laser that reaches the micropipette. The second parameter is the filament, where the user can select a range for the laser to scan over, or a scanning length. The following table lists the examples of scanning length of 6 different scanning patterns (table 3.4).

Filament #	Scan Length
0	1 mm
1	1.5 mm
2	1.9 mm
3	4.5 mm
4	6.5 mm
5	8 mm

Table 5.4 FILAMENT scan pattern values

The third parameter is the velocity. When the glass first begins to melt, the clamps holding it will begin to move apart due to the decreasing viscosity of the heated glass. This certain viscosity is a function of the glass temperature. As the temperature of the glass continues to rise, and the viscosity of the glass correspondingly decrease, the pipette pulls apart more rapidly until the velocity reaches the programmed value. When it reaches this programmed velocity value, trip point, the hard pull is initiated. In other words, the hard pull is initiated by the trip point which is defined by the velocity value. The fourth parameter is the delay between when the laser turns off and the pull begins. If the delay value is less than 128, the hard pull will be initiated before the deactivation of the laser (Figure 5.4). At delay value = 128, the hard pull is initiated at the same time as the deactivation of the laser. If the delay value is greater than 128, the hard pull will be initiated at the same time as the deactivation of the laser (Figure 5.5).



Figure 5.4 The delay value less than 128 millisecond.



Figure 5.5 The delay value greater than 128 millisecond.

Therefore a short delay value will pull the glass before there is any chance of cooling. The final parameter is the pull parameter. This simply controls the force of the hard pull.

5.1.3 Fabrication procedure using P-2000

The metal wire selected for the electrode probe is inserted into the 10 cm long glass capillary tube. This unit of capillary tube is loaded into the puller as follows [39] (Figure 5.6).

- 1) Loosen clamping knob.
- Place glass in V-groove in puller bar, slide it beyond clamp about 2 cm and tighten knob.
- 3) Depress the spring stop on each puller bar to release them from their catch position. (note: catch position is when the capillary tube is pulled into 2 piece.)
- 4) Pull both bars towards each other using the finger bars. Hold bars in position using the thumb and index finger from one hand. The hex head screw should be touching the end of the slot in both puller bars.
- 5) Loosen both clamping knobs and carefully slide glass through the holes in the side of the shroud and into V-groove of opposite puller bar.
- 6) Tighten down clamping knobs



Figure 5.6 Left puller bar of P-2000 micropipette puller.

After the glass tube is mounted on the puller, close the lid, and then press the PULL key on the keypad. The laser should turn on and the glass should be pulled with your designed program line (Figure 5.7). After the separation, loosen the clamping knobs and remove the pipettes from the puller bars.



Figure 5.7 Heat is applied by laser and pulling force is activate from both ends
5.1.4 Pulling steps

The pulling is normally divided into two steps. The first step is to pull the tube around the wire (Figure 5.8). The dimensions of the borosilicate glass capillary tube are outer diameter 1.0 mm and an inner diameter of 0.5 mm (the P-2000 is optimized for pulling tubes having outer diameter of 1.0 mm). The diameter of the gold wire is 50 μ m, thus the wire is 10 times smaller than the inner diameter of the tube. This gap between the wire and the glass must be decreased in order to transfer sufficient heat to the metal for the final pull, and thus the glass and metal form a composite material after the first pulling step.



Figure 5.8 First pull for making composite material.

The second step is the final pulling that separates the composite into two individual microprobes (Figure 5.9). The objective of the pull is to have the wire run continuously to the tip of micropipette. Yet, the tip of the pipette should be as small as possible. The probe tips are tapered down to submicron size. More specifically, the probe tip less than

300 nm is appropriate for the electrode probe used for electrical conductivity measurement.



Figure 5.9 Final pull

The tip of the microprobe is covered with the glass material, thus it should be etched with hydrofluoric (HF) acid. One part of the 50% HF was mixed with six parts of H₂O to obtain a solution with a glass etching rate of 120 nm/min. The glass material is borosilicate which is the amorphous form of SiO₂ containing: SiO₂: Na₂O: B₂O₃: Al₂O₃ (~75:7:12:6 by weight). After the tip of nanoelectrode is etched, it is inspected using a scanning electron microscope (SEM) (Figure 5.10), and the tip dimension is found to be approximately equal to 300 nm. (1 unit=250 nm)



Figure 5.10 SEM picture of gold nanoelectrode with the tip dimension of 300nm.

Here the elasticity of the composite material at the glass end (indicated with an arrow A-A in Figure 5.10) can be calculated using equation (2.17).

$$\begin{split} E_c &= \frac{E_m \left(d_m^2 - d_f^2 \right) + E_f d_f^2}{d_m^2} \\ &= \frac{64GPa \left(\left(2.5 \mu m \right)^2 - \left(1 \mu m \right)^2 \right) + 77.2GPa (1 \mu m)^2}{\left(2.5 \mu m \right)^2} \\ &= 66.11GPa \end{split}$$

The value of d_m and d_f are not the tip dimension but where the glass ends, thus d_f is 1 μ m. Thus the composite material elasticity was calculated at 66.1 GPa.

5.2 Other Fabrication technique to make microelectrode

In order to measure the electrical conductivity of small or fragile electronic materials, a MEMS microelectrode cantilever would be an ideal solution to make the task easier. Due to the fragility of both the sample and the probe tip, it is even better if electrode probe is designed in the form of a cantilever beam. The cantilever probe can be adjusted on the top surface of the sample gently while assuring the sample is not damaged. Before the purchase of the micropipette puller P-2000, a MEMS microelectrode cantilever fabrication technique using clean room facility was investigated.

To fabricate MEMS microelectrode cantilever probes through this lithographic technique, the following components were used:

- a) intrinsic silicon substrate (100) orientation
- b) positive photoresist (Shipley 1813)
- c) developer (MF-319)
- d) acetone (positive photoresist stripper)
- e) 1 photolithography mask for V groove
- f) HF glass etch solution (HF etch: $6:1 = H_2O: 50\%$ HF)
- g) KOH etch solution to make V groove in the Silicon substrate.
- h) Torr Seal epoxy to place the glass fiber in the V groove of silicon substrate.
- i) a solid glass fiber (with dimension of diameter = $50\mu m$)
- j) titanium source for metal evaporator
- k) gold source for metal evaporator

- l) 1 shadow mask
- m) four bolts
- n) sample holder for evaporator
- o) circuit board (2 holes for bolts)

5.2.1 Forming V-groove on the silicon substrate

The silicon substrate should be intrinsic so that it is electrically insulating under the room temperature environment. The silicon wafer was first oxidized in the oxidation furnace, so there was SiO_2 layer on top of the silicon substrate, which will be used as a mask for KOH etch. Before placing the wafer in the furnace, the wafer should be cleaned by rinsing with acetone, methanol, and deionized water in that order. The oxidation was followed by a dry technique in which the oxygen flows directly into the furnace tube, and then completed by a wet technique in which the oxygen was "bubbled" through a heated quartz flask containing deionized water. The reason for using those two oxidation technique is in the following: 1) dry oxidation grows oxide layer with great quality but the oxidation rate is very low compared to wet oxidation. 2) the oxide grown by wet oxidation has poorer quality, with less density, however the oxidation growing rate is excellent compared with dry oxidation. Thus in order to shorten the oxidation time, wet oxidation was followed by dry oxidation. It is important to operate dry oxidation first to create the thin oxide layer with good quality. Since it is the interface between oxide and silicon wafer, the intermediate oxide layer should be in good quality to increase adhesion between Si and SiO₂. In this experiment, dry oxidation was executed for 15 minutes and

it was followed by a wet oxidation for 2 hours at the furnace temperature of 1100 °C. The oxide thickness was calculated by the Deal-Grove Model formula [40]:

$$t_{ox}^2 + At_{ox} = B(t+\tau)$$
(5.1)

$$\tau = \frac{t_0^2 + At_0}{B}$$
(5.2)

Where t_{ox} is the oxide thickness, B/A is the linear rate coefficient, B is the parabolic rate coefficient (A and B have units of μ m and μ m²/hr), t is the oxidation time, t_o is the initial oxide thickness, and τ is the parameter to compensate for the rapid growth regime for thin oxide.

Tuble ble bly and wet exidation deetherents for sheeh.							
	Dry			Wet (640 torr)			
Temp (°C)	<i>A</i> (μm)	$B(\mu m^2/hr)$	t(hr)	<i>A</i> (μm)	$B(\mu m^2/hr)$		
800	0.370	0.0011	9	-	-		
920	0.235	0.0049	1.4	0.50	0.203		
1000	0.165	0.0117	0.37	0.226	0.287		
1100	0.090	0.027	0.076	0.11	0.510		
1200	0.040	0.045	0.027	0.05	0.720		

Table 5.5 Dry and wet oxidation coefficients for silicon.

According to the Deal-Grove coefficients table [41] above (Table 5.5), for dry oxidation at 1100 °C the coefficient of A, B, and τ , are 0.090 µm, 0.027 µm²/hr, and 0.076 hour respectively. The dry oxidation time t is 0.25 hour (15 minutes). By using these values in equation (5.1), oxide thickness t_{ox} is determined as 0.059 µm after dry oxidation. The τ for wet oxidation can be found by the equation (5.2), and the coefficients of A = 0.11 µm, and B = 0.510 µm²/hr for wet oxidation at 1100 °C and the initial oxide thickness t_o is 0.059 µm which is the oxide created by a dry oxidation. With these parameters, the value of τ is determined as 0.0196 hour. The wet oxidation time, t = 2 hr, so using these values to the equation (5.1), the final oxide thickness after the wet oxidation, $t_{ox} = 0.96$ um, which is approximately 1 µm. The oxide layer with the thickness 1 µm was sufficient for KOH etching mask in this procedure.

The silicon wafer was then broken into a rectangular shape with the dimensions of $1.5 \text{ cm} \times 2 \text{ cm}$ (Figure 5.11).



Figure 5.11 Cut silicon in rectangular shape

After breaking the wafer into small pieces, positive photoresist was spun coat on to the substrate (Figure 5.12) using 3000 rpm for 30 seconds. The substrate was then baked, in a "pre-bake" procedure (also called as a "soft bake" procedure) at 65~75 °C for 15 minutes to dry the photoresist.



Figure 5.12 Silicon substrate with photoresist coated

UV lithography light was then exposed through the mask (Figure 5.13 (a)). The following picture is the top view of how the mask was placed on top of the silicon wafer (Figure 5.13 (b)).



Figure 5.13 (a) UV lithography side view, (b) UV lithography top view

Next, the photoresist was patterned in a developer solution MF-319 (Figure 5.14 (a)). The period of immersion was about 50 seconds. The developer acts as a solvent which removes the u.v. exposed, positive resist. During this process, the wafer was checked to avoid over developing. After developing (Figure 5.14 (a)), the wafer was rinsed with running deionized water (DI) to terminate the developer stage of this procedure, and a post-baking step is used to further harden the photoresist. The post-bake procedure or also called as a hard bake procedure, was executed in the oven at 120 °C \pm 5 °C for 15 minutes. Next the underlying silicon dioxide layer was etched using a hydrofluoric acid (HF) (Figure 5.14 (b)). The HF solution was prepared by mixing 6 parts of H₂0 and 1 part of 50% HF, which gave an etching rate of typically about 1200 Å/min (120 nm/min). In order to etch 1 µm oxide layer, the HF etching time should be a little longer than 8 minutes. The photoresist mask was removed by acetone, leaving a mask of SiO₂ as shown in Figure 5.14 (c).



Figure 5.14 (a) Photoresist developing, (b) Patterning oxide layer, (c) Stripping photoresist.

The silicon substrate was then anisotropically etched (Figure 5.15) by a KOH solution [42].



Figure 5.15 Silicon anisotropic etching [42].

The KOH is an anisotropic etchant for silicon such that it etches at different rates along different crystal orientations. Silicon structure has three primary planes (100), (110), and (111) in the Miller representation. Anisotropic silicon etching occurs because these different planes represent a different density of silicon atoms to the etchant as each plane is exposed and exhibit different surface bonding configurations for each plane. In (100) plane, the atom has two dangling bonds while (111) has three. Thus it is much easier to take a silicon atom in (100) plane orientation than (111) plane. In this reasoning, with KOH anisotropic etchant, (100) surface etches faster than (111) surface. Therefore the V

grooves were created in the silicon wafer by KOH etching (Figure 3.16), and its top view is shown in Figure 5.17.



Figure 5.16 V-grooves created by KOH etching.

The KOH solution can be prepared by mixing 50g of KOH, 100ml of H_2O , and 50ml of methanol [43], and should be used at a temperature of 85 °C. This temperature was maintained by keeping the solution on a hot plate. The etching time was determined as 1 hour 42 minutes, and the calculation is shown in the next subsection. After the KOH etching, silicon oxide mask was removed by a HF solution (Figure 5.17).



Figure 5.17 (a) The top view of V-groove after removing oxide. (b) The side view of V-groove after removing oxide mask.

5.2.1.1 Etching time calculation

The V groove in this experiment will have a width of 80 μ m, and the anisotropic etch of silicon at a (100) orientation gives an angular profile of 54.74 ° (Figure 5.15). According to the triangle relation's as seen from the (Figure 5.18), the groove depth can be calculated:

$$\tan 54.74^{\circ} = \frac{x\mu m}{100\mu m}$$
(5.3)

$$x = 141.4 \,\mu m$$

Thus, 141.4 μ m is the depth that needs to be etched. The etching rate of silicon wafer by the KOH solution is 1.38 μ m / min along the (100), direction. Multiplying the etching rate by the undetermined time of etching gives the etching depth which equals 141.4 μ m. The etching time follows from the calculation bellow:

$$1.38\,\mu m \,/\,\min \times y \min = 141.4\,\mu m$$
 (5.4)

 $y = 102.5 \min$

Therefore, the KOH silicon etching time is 1 hour 42 minutes 30 seconds.



Figure 5.18 Triangle relations on the V-groove

5.2.2 Preparing the glass fiber metal evaporated electrode probe

A Pyrex glass fiber with diameter of 50 to 100 μ m was cut in pieces and glued into V-groove traces of silicon wafer using Torr Seal epoxy. Torr Seal epoxy resin is conventionally used to seal leaks on any type of vacuum system or components. It is solvent-free and can be used at pressure of 10⁻⁹ Torr and below, and temperatures from 45 °C to 120 °C [44]. Since the wafer with glass fiber was placed in the evaporator where the chamber was vacuumed, to be coated with some metals later, the Torr Seal was suitable as a epoxy to hold the glass fiber into the V-groove created in silicon wafer. Here the temperature allowance range for Torr Seal is up to 120 °C. In the metal evaporator, the crucible containing metal sources requires an extremely high temperature in order to boil/evaporate those designated metals; however, around the target/sample area where the metal is coated does not need as high temperature as in the crucible. Due to these reasons, Torr Seal epoxy was selected.

Small amount of the epoxy can be placed in the grooves, followed by the optical fibers. The lengths of fiber cantilever beams were aligned by putting a ruler against the end of the fibers before the epoxy dries/cures (Figure 5.19).



Figure 5.19 The glass fibers mounted on V-groove (a) Top view, (b) Side view

After the glass fibers were carefully mounted on the grooves of silicon wafer, the unit was mounted and placed in the evaporator. The sample was covered with shadow mask (Figure 5.20) and screwing down with bolts to the sample holder. The sample holder was then mounted on the lid of the metal evaporator where was directly above the metal boat. A titanium source and a gold source were placed into the boat and chamber was closed to acquire a specific vacuum environment for each metal to evaporate.



Figure 5.20 Sample covered with shadow mask for metal evaporation (a) Top view, (b) Side view

First titanium was deposited by metal evaporation technique. The goal here was to deposit patterned gold metal on the grooves to make electrical connections for four-point probe. Gold was preferred due to its non-oxidizing properties and its low resistivity ($\rho = 2.26 \ \mu\Omega cm$ at T = 298 K). However, gold does not exhibit good adhesion to SiO₂, therefore an intermediate layer such as chromium is often used which has significantly better adhesion properties with SiO₂. The coefficient of thermal expansion (CTE) of gold (14.2 × 10⁻⁶ /K) and silicon dioxide (0.4 × 10⁻⁶ /K) has a significant difference, so that it is recommended to introduce an intermediate layer before the gold deposition to enhance the adhesion. There are several candidates for intermediate layers including titanium,

tungsten, nickel, and chromium. And titanium was selected as an intermediate layer due to the availability at the Keck Microfabrication Facility located in the Physics and Astronomy Department at Michigan State University. Moreover, the CTE of titanium is 8.6×10^{-6} /K, which is somewhat in between values for silicon dioxide and gold. Coefficient of Thermal expansion α is defined as, $\alpha_T=d\epsilon_x/dT$. Metal films deposited on SiO₂ expand at different rates as the temperature changes. Those films are deposited at high temperature, and the sample are taken out and cooled down at room temperature. When the substrate is cooled down, some stress develops in the thin film due to this mismatch in expansion/contraction. Thus as temperature changes strain builds up in the material, which can lead to bend (or curled) cantilevers.

$$\varepsilon_x(T) = \varepsilon_x(T_0) + \Delta T \qquad (5.5)$$

Before the metal evaporation, the evaporator chamber needs to acquire certain vacuum environments for specific metal evaporation run. Evaporation requires the chamber environment to be 5×10^{-7} Torr. The evaporation can be done consecutively if the evaporator allows more than one boat in the chamber with appropriate shutter. At the Keck facility, the evaporation chamber has four boats with a shutter above, and thus there are four options for metals at most. The vacuum environment was acquired with two pumping systems called rough pump and turbo pump. The rough pump is capable of pulling a vacuum down to about 1×10^{-3} Torr. High vacuum pump such as turbo pump can further reduce the pressure to approximately 1×10^{-6} Torr to 1×10^{-8} Torr. Thus the rough pump was operated first until acquiring 1 mTorr, and after such an environment

was retained the turbo pump took over the rough pump for finalizing the vacuuming process.

When the chamber acquired the certain vacuumed environment, the metal evaporation can proceed. The evaporation was done by heating the boat which contained metal inside. The both ends of boat were connected to electrodes and the current was passed through the boat to resistively heat the boat by joule heating. A pre-deposition heating of the metal source was used to remove contamination from the metal source and the boat. After this step, the shutter between the metal source and the sample was opened for the deposition step. The boiling point of titanium and gold are 3287 °C and 2856 °C respectively [45], so it needs a higher value on the current control switch for titanium to start evaporating it. The titanium layer of thickness = 10 Å was first deposited (Figure 5.21 (a)), and the gold layer of thickness = 30Å was deposited as a following step (Figure 5.21 (b)) in the evaporator. As a result, the gold metal was coated over the cantilever beam with a intermediate layer of titanium (Figure 5.21 (c)).



Figure 5.21 (a) Titanium deposition, (b) Gold deposition, (c) final look after metal depositions

This fabricated MEMS four-point probes can be then mounted on the xyz translation stage, and the resistivity of the semiconductor sample can be measured by the probes (Figure 5.22).



Figure 5.22 The circuit of fabricated four point probe.

5.2.3 Results

Although this fabrication technique was planned originally, there were few difficulties encountered during the fabrication process. During the preparation of making V-groove, the oxidized silicon wafer should be coated with photoresist on both front and backsides. Since the normal silicon wafer has a thickness of 500 μ m or less, the KOH anisotropic etching thinned silicon substrate and made it fragile if the back side of the wafer were not covered with oxide layer. In the furnace, oxide layers were grown both front and backside, and both layers should be a mask for KOH etching. Therefore the photoresist should be coated on both sides. First, the entire top surface of substrate was covered with photoresist, and then the substrate was placed in the oven for prebake. The wafer was then turned over and mounted on spin coater. The backside of the silicon wafer was coated with photoresist in advance. This proved to be challenging, since when the spincoater started to spin the substrate, the vacuum system activated and pulled vacuum on the photoresist coated side of the wafer which damaged the photoresist coating on the backside.

The front side is extremely important, since the v-groove pattern is done by lithography on the front side. For a better photoresist film on the front side, the front side was processed only after the backside was completed. Damage to the backside photoresist layer continued to allow significant KOH etching of the substrate and resulted in fragile substrates.

In the second trial after above problem had been encountered, the V-groove creation was discontinued. Instead of coating the whole unit with metal sources, the individual components, silicon substrate and the fiber, were coated with metals first and glued (with electrically conducting adhesive) together in the end. This technique met with limited success after significant effort was made in aligning the fiber to the metal pattern created on silicon surface.

In addition to the difficulties of the fabrication procedure by clean-room method, the size of the probe tip was limited. Since the normal glass fiber of diameter 50 μ m without tapering was used as a probe, the tip dimension was limited at the micron size. However, with the use of the P-2000 micropipette puller, the probe tip size can be drawn in sub micron size (unfilled glass tubes have been pulled down to 17 nm in diameter and wire filled tubes down to ~100 nm have been fabricated) extending our capabilities. This enables to probe not only the small structured sample but also the small sample with doping profiles within the extremely localized area. In addition, this technique results in insulated probes such that thermocouple probes or multifunctional probes can be envisioned. The reduction in exposure to, and use of hazardous chemicals in this technique is also a desirable result.

6. DATA ANALYSIS

6.1 One-point probe scanning measurement method

To test the submicron-electrode, the electrical conductivity of a sample of Bi_2Te_3 , copper, and graphite was measured using the one-point probe method. Conventional methods of measuring electrical conductivity include the four-point probe method and the two-point probe method. We have developed a new technique for our lab that uses only one probe to scan the length of the semiconductor material. This allows the measurement, not only of the conductivity of the sample, but also of the contact resistance at the interface of the semiconductor and the metal.

In the four-point probe and the two-point probe methods a constant probe spacing is employed. The constant probe spacing enables the simple calculation of conductivity according to the formula shown below:

$$\sigma = \frac{ll}{VA} \tag{6.1}$$

where σ is the conductivity, *I* is the current, *l* is the probe spacing, *V* is the voltage and *A* is the cross-sectional area of the sample.

The four-point probe method has two outer probes where the current source is applied to the sample, and two inner probes where the voltage difference is measured. Similarly, the two-point probe method also features a set of inner probes that measure the voltage difference. However, in this case the current is applied from the edges of the semiconductor material through a metal contact. The thin metal contact is created either by sputter coating, metal evaporation, or electrochemical deposition. In both probe methods, since the voltage is measured between the two inner probes, the contact resistance is not included. Thus, the one point probe method has the advantage of detecting the voltage drop at the contact resistance. This allows the further study of the contact resistance and helps to improve and make better contact with appropriate metals.

6.1.1 The probe mounting angle calculation

In order to verify the probe mounting angle, the maximum deflection formula was used. In chapter 2, the maximum deflection formula was combined with a trigonometric formula and, it was simplified as equation (2.25). In order to find the optimum angle, the force applied, the tapered length of the nanopipette, L, and the average radius of the tapered region, r, have to be estimated.

For a commercialized Hall measurement probe, the force on a 5 mil (127 μ m) radius of the probe tip is rated at 50 gram [46].

The pressure from the probe is:

$$\frac{Force}{TipArea} = \frac{50g}{\pi (127\,\mu m)^2} \tag{6.2}$$

In our case, we have a cantilever beam with a tip diameter of 250 nm. So the tip radius is 125 nm; hence, for the same pressure the approximate force to be applied to our cantilever is:

$$\frac{50g}{\pi (127 \mu m)^2} = \frac{F}{\pi (125 nm)^2}$$

F = 4.84×10⁻⁵ g

The unit of Ec, the composite material elasticity is converted to SI units: from GPa to

g/m²:
$$Ec = 66.1 \times 10^9 \operatorname{Pa}\left(\frac{10^3}{9.8} \frac{g/m^2}{Pa}\right) = 6.73 \times 10^{12} \text{ g/m}^2$$

The tapered length of the nanopipette is approximately: L=4 mm.

Since the cantilever radius is not consistent, the averaged radius of the tapered region is estimated as follows. In the assumption, the tapering starts when the glass diameter is approximately equal to 10μ m, and the tapering region ends at 250 nm (tip diameter). Assuming the tapering occurs at linear rate (Figure 6.1), the formula is established as follow:

$$y = slope \times x + 125nm$$

= $\frac{(5\mu m - 125nm)}{4mm}x + 125nm$ (6.3)
 $y_{x=2mm} = 2.56\mu m$

Thus cantilever radius is: $r = 3 \mu m$.





$$\tan \theta = \frac{4FL^2}{3E_c \pi r^4}$$

$$\theta = \tan^{-1} \left(\frac{4FL^2}{3E_c \pi r^4} \right)$$

$$= \tan^{-1} \left(\frac{4(4.84 \times 10^{-5} g)(4 \times 10^{-3} m)^2}{3(6.73 \times 10^{12} g / m^2) \pi (3 \times 10^{-6} m)^4} \right)$$

$$= 31.09^\circ$$

These calculations verify a probe mounting/ deflection angle of 30° is appropriate.

6.2 DC sweeping current source using Keithley 2400 source meter

6.2.1 Bi₂Te₃

First, the edges of the Bi_2Te_3 sample were coated with nickel by electrochemical deposition to form the electrical contacts. I- (ground) and V- leads are connected to the metal contact on the left, and the I+ lead is connected to the metal contact on the right side of the semiconductor. The gold electrode probe with a tip dimension of 300 nm is mounted on an *xyz*-translation stage at an angle of 30° with respect to the sample. The sample is sourced by sweeping 10mA using 2400 source meter from Keithley Instruments [47] (Figure 6.2).



Figure 6.2 DC conductivity measurement system set up[48].

The electrode scans the length of the sample from left to right. Both probe spacing, l, (in this case, the distance of the electrode from the left metal plate) and the voltage

difference, V, increase as the electrode scans the surface (Figure 6.3). The voltage difference is measured by 2182 nanovoltmeter [49] from Keithley Instruments.



Figure 6.3 Sample set up.

Since the metal contact is included in the probe spacing area, the voltage drop (or contact potential) at the metal contact is added to the voltage measured when the probe is scanned. When l = 0, only the contact potential is measured, and then the voltage increases linearly with l. The data taken from the measurement is listed in Table 6.1 and shown graphically in Figure 6.4.

Probe spacing	Voltage drop	Voltage drop	Voltage drop			
	(1 st run)	$(2^{nd} run)$	(3 rd run)			
0	5.6 µV	5 μV	4.85 μV			
1	129 µV	140 µV	203 µV			
2	136 µV	165 µV	228 µV			
3	137 µV	156 µV	225 µV			
4	140 µV	173 μV	213 μV			
5	141 µV	181 μV	224 μV			
6	144 μV	187 μV	224 μV			
7	147 μV	188 µV	232 μV			
8	150 μV	198 µV	235 µV			
9	155 μV	200 µV	242 μV			
10	153 μV	203 µV	245 μV			
11	156 µV	205 µV	256 μV			
12	167 μV	208 µV	250 μV			
13	170 µV	211 μV	253 μV			
14	175 μV	194 µV	258 μV			
15	179 μV	186 µV	260 µV			
16	183 µV	189 µV	282 μV			
17	187 µV	191 µV	280 μV			
18	189 µV	212 μV	310 μV			
19	194 µV	213 μV	316 µV			
20	194 µV	213 μV	300 μV			
21	450 μV	574 μV	583 μV			

Table 6.1 Data of scanned voltage difference on Bi₂Te₃ sample using DC technique.

Contact resistance of the Nickel plating is calculated as follows.

$$\sigma_{contact R} = \frac{(0.129 - 0.0056)mV}{10mA} = 12.3 m\Omega$$

$$\sigma_{contact R} = \frac{(0.45 - 0.194)mV}{10mA} = 25.6 m\Omega$$

The differential voltage was taken from the data acquired at 1st run.



Figure 6.4 Plot of scanned voltage difference on Bi₂Te₃ sample using DC technique.

To calculate the electrical conductivity, the slope of the linear region has to be determined. The plot is linearized by KaleidaGraph software and the function including a slope of the line is determined (Figure 6.5). The slope of the plot is inversely related to the electrical conductivity of the sample, and the formula is shown below:

$$\sigma = \frac{I\Delta l}{\Delta VA} \qquad (6.4)$$



Figure 6.5 Plot of the linear region of scanned voltage difference on Bi₂Te₃ sample using DC technique.

The slope of each linear fit gives the value of $\left(\frac{\Delta V}{\Delta l}\right)$ for use in equation (6.4)

 Δl is simply the difference between the final probe location and the initial location: 0.456cm.

The dimensions of the Bi₂Te₃ are: width (w) = 0.445cm, thickness (t) = 0.22 cm, length (l) = 0.525cm, thus the electrical conductivity of the Bi₂Te₃ is calculated as follows:

$$\sigma_{1} = \frac{10mA}{(0.14799mV/cm)[(0.445cm)(0.22cm)]} = 690S/cm$$

$$\sigma_{2} = \frac{10mA}{(0.1093mV/cm)[(0.445cm)(0.22cm)]} = 934S/cm$$

$$\sigma_{3} = \frac{10mA}{(0.20356mV/cm)[(0.445cm)(0.22cm)]} = 483S/cm$$

$$\sigma_{average} = \frac{690 + 934 + 483}{3} = 702S/cm$$

Thus the electrical conductivity of the Bi₂Te₃ is: 702 S/cm

6.2.2 Aluminum foil

To test the gold electrode probe further, aluminum foil is used as the secondary sample. Metal has much higher electrical conductivity than semiconductor, and this makes it difficult to detect the increment in voltage with a scanning probe. In order to increase the total resistance of the aluminum, the foil is cut in long strip with the smallest width possible. The aluminum foil is cut with a width of 4.1 mm, a length of 20.9 mm, and a thickness of 0.02 mm as measured by Vernier calipers. Total resistance of this aluminum sample is calculated by the following:

$$R_{total} = \rho \frac{l}{A}$$
$$= 2.67 \mu \Omega cm \frac{2.09 cm}{(0.41 cm)(0.002 cm)}$$
$$= 6.8 m \Omega$$

If $I = \pm 50$ mA is swept, the voltage across the aluminum is:

$$V_{al} = IR = 340 \mu V$$

Thus the voltage increment from l = 0 mm to l = 20.9 mm should be 340 μ V, and the value is large enough to be detected by a nanovoltmeter. It was discovered that these

small probes can be easily damaged on harder surfaces such as aluminum, however, surface contaminants such as oxides require greater pressure on the probes to break through the contaminant layer. Because of this, the data was not as stable as with the previous sample. To strengthen the tips, a coating of silver paste at the tip was investigated. This significantly enhanced the signal quality, by not only strengthening the probe tips, but also by decreasing the contact resistance to the sample. However, in order to achieve the original goal which was the fabrication of a submicro-electrode probe to characterize the electrical conductivity of an extremely localized area, the probe was tested without applying silver paste as an enhancement.

The problems listed above are all due to the extreme small dimension, (~300nm) of the probe tip. To help avoid damage to the probes, a microscope was used during the measurement; however, the data still showed instability even if the cantilever is deflecting and contacting to the sample surface. In order to see this problem, the conduction is tested by using multi-meter. The electrical conduction was tested by clipping the V+ wire end, the wire connected to the nanoelectrode, and touching the aluminum surface while the nano electrode made the contact to the sample (Figure 6.6).



Figure 6.6 The electrical conduction test of submicron probe.

The conduction was not stable, and it alternated on and off rapidly. This resulted in unacceptably noisy data. The contact is not consistently made, and therefore the nanovoltmeter could not read a stable voltage value. One of the reasons might be artifacts due to improper vibration isolation. Since the probe is extremely small, it is very sensitive to even a small vibration. Furthermore, the nanoelectrode might have caught some other noise signal (e.g. electromagnetic wave) from the environment. In order to enable a more precise measurement, the electrode is employed using an AC source with a noise filtering feature using EG&G 7265 DSP Lock-in amplifier. The set up of the system is explained in the following section.

6.3 AC source using EG&G 7265 DSP (Digital Signal Processor) Lock-In Amplifier

In this section, it is described how we built an AC conductivity measurement system using EG&G 7265 DSP lock-in amplifier. Before the system set up is explained the basic concept of the lock-in Amplifier is reviewed.

6.3.1 Lock-in Amplifier

In its most basic form, the lock-in amplifier is an instrument with dual capability. It can recover signals in the presence of an overwhelming noise background or, alternatively, it can provide high-resolution measurements of relatively clean signals over several orders of magnitudes and frequency. A common problem has arisen while detecting and measuring the amplitude of an electrical signal in the presence of muchlarger-amplitude, random, electrical noise. This electrical noise covers a wide band of frequencies. The lock-in amplifier is a powerful device for filtering out the unwanted noise by utilizing a phase-sensitive detection method.

A lock-in amplifier uses phase-sensitive detection to improve the signal-to-noise ratio in a common experiment. The measured input signal will include an analytical signal and the other noise signals. Using phase-sensitive detection requires the analytical signal to be modulated at some reference frequency. The lock-in-amplifier then amplifies only the component of the input signal at the reference signal, and filters out all other frequencies (e.g. noise). Thus, the demodulator operates by multiplying these two signals together to yield the "demodulator output".

Input/measured signal × reference signal = demodulator output

$$A\sin(wt+\phi)*B\sin(wt) = \frac{AB}{2}\cos\phi + \frac{AB}{2}\cos(2wt+\phi) \qquad (6.5)$$

Since there is no relative phase-shift between the input signal and reference phases (e.g. $\phi=0$) the demodulator output takes the form of a sinusoid at twice the reference frequency, but with a mean, or average, level which is positive (Figure 6.7). The mean level is the DC component of the demodulator output, so it is a relatively simple task to isolate it by using a low-pass filter. Since the reference signal amplitude is fixed, and the reference phase is adjusted to ensure a relative phase-shift of zero degree, the input signal amplitude can be determined by measuring the mean level.



Figure 6.7 The demodulation of two signals [50]

The above discussion is based on the case of noise-free input signals, but in real applications the signal will be accompanied with noise. This noise, which by definition has no fixed frequency or phase relationship to the reference, is also multiplied by the reference signal in the demodulator. However, this does not result in any significant change to the mean DC level, due to its different frequency set. Noise components at frequencies very close to that of the reference do result in demodulator outputs at very low frequencies, but by setting the low-pass filter to a sufficiently low cut-off frequency

these can be rejected. Hence the combination of a demodulator and low-pass filter can be used to monitor signals at a given frequency.

6.3.2 Setup procedure using EG&G 7265 DSP (Digital Signal Processor) Lock-In Amplifier

The basic concept of lock-in amplifier was discussed in the previous section. In our application, the internal reference signal was utilized to measure the signal having the same frequency as the output oscillating sinusoidal signal.

The experimental setup with the lock-in amplifier is explained in the following. First the sample was mounted on a circuit board, and the gold nanoelectrode probe was mounted on the xyz translation stage at an angle of 30° with respect to the sample. The wires were soldered to both ends of the copper strip and the oscillating sinusoidal signal was sourced to the sample using EG&G 7265 DSP (Digital Signal Processor) Lock-In Amplifier [51]. To monitor the value of current applied to the sample, a 1 Ω resistor was connected in series with the sample as shown in Figure 6.8. The current was determined by measuring the voltage across the 1 Ω current sense resistor using the lock-in amplifier. The voltage across this sense resistor was measured by the lock-in amplifier using the differential measurement mode with both A and B channels. Since the resistor value is 1 Ω , the current sourced to the sample is simply equal to the measured voltage across the resistor.



Figure 6.8 Lock-in amplifier set up to determine the current of the system

After measuring the value of current, the voltage difference between the probe (V+) and the V- was measured using the lock-in amplifier with a signal channel input node A and ground (Figure 6.9). The probe was then scanned from the side I- to I+, and thus the voltage should linearly increase from l=0 to l=L.



Figure 6.9 Lock-in amplifier set up to measure the scanned voltage of the sample.

A photograph of the AC conductivity measurement system is shown in Figure 6.10.



Figure 6.10 Lock-in amplifier set up picture

As a first trial, a frequency of 50 Hz, and an amplitude of 2 V rms signal was sourced to a copper strip. The voltage across the resistor was measured with the value, 34.19 mV, and thus the source current with this setting is I = 34.19 mA. However the voltage measured by the nanoelectrode probe was not stable. In order to improve the signal, an oscilloscope was used to monitor the signal in the circuit. The signal was inspected at the point A in the circuit using the oscilloscope. The signal captured by the oscilloscope was not a pure sinusoidal wave, but exhibited cropping of the sinusoidal extrema. It was speculated that the compliance current of the lock-in Amplifier exceeded the limit, and thus the signal was not a pure sinusoidal curve. In order to get a more stable signal, the amplitude of the oscillating voltage signal was reduced to 1 V rms. With the lowered rms voltage, the signal captured at the point A became sinusoidal. This
was found to be very important step that significantly improved the measured signal quality and is recommended for each sample measured.

6.3.3 Copper strip

Utilizing a 1 V rms oscillator signal at 150 Hz is the circuit shown in Figure 6.9, the measured voltage across the 1 Ω resistor was 19.28 mV, which indicated a source current of 19.28 mA. To test the probe measurements, the total resistance of copper strip and the entire circuit resistance were measured in an independent measurement system using a Keithley 2400 source meter and 2182 nanovoltmeter. The sweep current of 1mA was sourced to the copper strip and the voltage drop was measured as 0.0217 mV by the nanovoltmeter. The total resistance including the current lead wires [constantan wire (50 µm diameter)] and the interface resistance of the solder to the copper strip was also measured (0.816 mV for 1mA source current). By taking ratio of V/I, the total resistance of the copper strip, and of the entire circuit was measured to be 21.7 m Ω and 0.816 Ω respectively. The large increase in impedance of the entire circuit is due to the constantan wire with the small cross sectional area. The dimensions of copper strip are: thickness = 0.002 cm, width = 0.158 cm, and length = 3.763 cm. The resistivity of copper at the room temperature is 1.72 $\mu\Omega$ cm [52]. Thus the total resistance of the copper is calculated as:

$$R_{total} = 1.72 \mu \Omega cm \frac{3.763 cm}{(0.002 cm)(0.158 cm)}$$
$$= 20.48 m \Omega$$

Thus the percentage error is:

$$\% error = 100 \times \frac{R_{measured} - R_{calculated}}{R_{measured}}$$
$$= 100 \times \frac{21.7m\Omega - 20.48m\Omega}{21.7m\Omega}$$
$$= 5.62\%$$

Now the circuit is analyzed as follows. First the rms voltage value of the lock-in amplifier was verified using the oscilloscope (Figure 6.11). A BNC cable was connected to the oscilloscope and the output oscillating signal was captured.



Figure 6.11 Oscilloscope connected to the output of lock-in amplifier.

The peak of the signal captured was 1.5 V and the rms value of the signal was calculated by:

$$V_{rms} = \frac{Peak}{\sqrt{2}}$$
$$= \frac{1.5V}{\sqrt{2}}$$
$$= 1.06V_{rms}$$

The value is reasonable since the lock-in amplifier is sourcing 1 V rms oscillating signal. In the next step, the voltage of the nodes A and B in the circuit (across the resistor) are captured by the oscilloscope as the channel 1 and 2 respectively (Figure 6.12).



Figure 6.12 The signals captured by Oscilloscope: A) channel 1 B) channel 2 (20 mV/div)

The rms values of the nodes A and B are calculated and the voltage difference is obtained

as follows:

$$V_{preskA} = 2.6_{div} \times 20mV / div = 52mV$$

$$V_{preskB} = 1.2_{div} \times 20mV / div = 24mV$$

$$V_{maxA} = \frac{52mV}{\sqrt{2}} = 35.78mV_{ma}$$

$$V_{rmsB} = \frac{24mV}{\sqrt{2}} = 16.97mV_{rms}$$

$$V_{accossID} = v_{rmsA} - V_{rmsB} = 35.78mV_{rms} - 16.97mV_{rms}$$

$$= 18.8 ImV_{rms}$$

The value measured here verifies that the voltage difference of 19.28 mV (A-B) taken by lock-in amplifier is reasonable. The discrepancy is due to the approximated estimation of the division at the peak of the real signal obtained by oscilloscope.

The total resistance of the circuit board is measured at 0.816Ω by the nanovoltmeter, so the voltage drop across the circuit would be (Figure 6.13): 19.28 mA × $0.816\Omega = 15.73$ mV. Including the voltage drop across the resistor, the total voltage difference is: 35.01mV. Since lock-in amplifier is sourcing 1 V rms voltage, there is some voltage drop at the internal impedance of the oscillator: 1 V - 35.01 mV = 0.965 V. The internal impedance of the lock-in amplifier is: $0.965 \text{ V} / 19.28 \text{ mA} = 50.05\Omega$. This value is verified by the hardware manual of EG&G 7265 DSP (Digital Signal Processor) Lock-In Amplifier: Output oscillator impedance = 50Ω .



Figure 6.13 Lock-in amplifier circuit analysis

In order to test the one-probe scanning conductivity measurement system with lock-in amplifier, bigger probes were employed. These are listed below: 1) a gold coated pin with 500 μ m diameter (large dimensioned probe). 2) A Pt wire with 50 μ m diameter

(intermediate dimensioned probe). The data successfully acquired using these probes was

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tabulated (Table 6.2) and plotted (Figure 6.14) in the following.

teeninge	te une pin proce une re win	e proce.
Probe spacing (l)	Scanned voltage	Scanned voltage
	(500 µm diameter pin)	(50 µm Pt wire)
0	11.31 mV	11.63 mV
1 mm	11.32 mV	11.63 mV
2 mm	11.33 mV	11.63 mV
3 mm	11.33 mV	11.65 mV
4 mm	11.34 mV	11.65 mV
5 mm	11.35 mV	11.68 mV
6 mm	11.35 mV	11.70 mV
7 mm	11.36 mV	11.73 mV
8 mm	11.37 mV	11.74 mV
9 mm	11.38 mV	11.76 mV
10 mm	11.40 mV	11.78 mV
11 mm	11.42 mV	11.79 mV
12 mm	11.44 mV	11.81 mV
13 mm	11.45 mV	11.83 mV
14 mm	11.47 mV	11.79 mV
15 mm	11.48 mV	11.81 mV
16 mm	11.51 mV	11.83 mV
17 mm	11.52 mV	11.85 mV
18 mm	11.54 mV	11.86 mV
19 mm	11.56 mV	11.87 mV
20 mm	11.57 mV	11.90 mV
21 mm	11.58 mV	11.91 mV
22 mm	11.60 mV	11.93 mV
23 mm	11.61 mV	11.94 mV
24 mm	11.63 mV	11.96 mV
25 mm	11.64 mV	11.97 mV
26 mm	11.66 mV	11.98 mV
27 mm	11.67 mV	11.99 mV
28 mm	11.68 mV	12.01 mV

Table 6.2 Data of scanned voltage difference of copper using ACtechnique and pin probe and Pt wire probe.



Figure 6.14 Plot of scanned voltage difference of copper using AC technique and pin probe and Pt wire probe.

The voltage difference across the sample is: $\Delta V_1 = 11.696 \text{ mV} - 11.284 \text{ mV} = 0.412 \text{ mV}$.

$$\Delta V_2 = 12.059 \text{ mV} - 11.612 \text{ mV} = 0.447 \text{ mV}.$$

The expected voltage difference across the sample is as following: $19.28 \text{ mA} \times 21.7 \text{ m}\Omega$ = 0.42 mV. The conductivity of the copper sample is calculated as follows:

$$\sigma_{pin} = \frac{(19.28mA)}{(0.01472mV / mm \times 10mm / cm)(0.002cm)(0.158cm)} = 415 \text{ kS / cm}$$

$$\sigma_{Pt wire} = \frac{(19.28mA)}{(0.015955mV / mm \times 10mm / cm)(0.002cm)(0.158cm)} = 382 \text{ kS / cm}$$

The electrical conductivity of copper is the reciprocal of the resistivity: $\sigma_{copper} = \frac{1}{1.72 \mu cm}$

= 581 kS/cm. The measured conductivity by the one-point probe is lower than the standard. The cross sectional area of the copper sample was measured under a microscope; however, the thickness might vary in each location due to the surface treatment. (The surface of the copper strip was polished to improve the smoothness.) The measured conductivity seems to have a little offset due to this inconsistent cross sectional area dimension.

After the system was verified with the larger probes, the small probe (tip dimension = 700 nm) is now employed. First, the pulled quartz pipette coated with gold is used as the nanoelectrode probe (Figure 6.15).



Figure 6.15 SEM picture of gold nanoelectrode

The gold material is sputter coated for 2 minutes (sputter coating rate = 7 nm/min), thus the gold coating is approximately equal to 14 nm. It was extremely difficult to make a contact to a sample with the nanoelectrode; and thus, the probe need to be deflected significantly in order to take data. Fortunately, the nanoelectrode had a long tapered neck, enabling it to deflect a large degree. The required deflection to acquire data depends on the location of the sample measured. Therefore, it is speculated that, some parts of the sample suffered topographical roughness or oxidation. However, even with a large amount of deflection, the probe could not make a good contact at some locations on the sample. In these cases, the probe was repositioned slightly in the x and y direction to make a better contact. With this effort, data acquisition was completed (Table 6.3) (Figure 6.16). Due to the extended length of this process, the data sometimes decreased abruptly as an offset. This occurred at the transitions of $l = 10mm \sim 11mm$, and l = $17mm \sim 18mm$. Therefore the conductivity of the copper is now taken by averaging those 3 data sets (slopes) as follows:

$$\sigma_{1} = \frac{(19.28mA)}{(0.082727mV / cm)(0.002cm)(0.158cm)} = 738kS / cm$$

$$\sigma_{2} = \frac{(19.28mA)}{(0.17143mV / cm)(0.002cm)(0.158cm)} = 356kS / cm$$

$$\sigma_{3} = \frac{(19.28mA)}{(0.12061mV / cm)(0.002cm)(0.158cm)} = 506kS / cm$$

$$\sigma_{i} = \frac{(\sigma_{1} + \sigma_{2} + \sigma_{3})}{3} = 533kS / cm$$

Soonnad valtage (mV)
12.00 mV
13.20 mV
13.20 mV
13.21 mV
13.21 mV
13.22 mV
13.23 mV
13.24 mV
13.26 mV
13.26 mV
13.26 mV
13.28 mV
13.19 mV
13.21 mV
13.22 mV
13.24 mV
13.26 mV
13.28 mV
13.29 mV
12.83 mV
12.85 mV
12.86 mV
12.88 mV
12.89 mV
12.91 mV
12.92 mV
12.92 mV
12.93 mV
12.94 mV

 Table 6.3 Data of scanned voltage difference of copper using AC technique and gold nanoelectrode.



Figure 6.16 Plot of scanned voltage difference of copper using AC technique and gold submicron electrode (d=700nm).

6.3.4 Graphite sample

In order to protect the tip from damage, a soft sample such as graphite was used for the measurement. Also a Pt microelectrode was used here to make a strong contact without causing any damage.

The pulled gold nanoelectrode was tested on a copper sample as discussed previously; however, the data was unacceptable due to problems of poor contact. It was speculated that since gold is a soft material (when compared with other metals) it was not able to tolerate the contact pressure imposed on tip of small dimensions (700 nm). Thus, a platinum microelectrode was used instead. However, the tip of the Pt electrode dimension was larger than the gold nanoelectrode. This was due to its material hardness, that made it difficult to make a fine taper. The tip diameter of the Pt microelectrode measured under a microscope in a cleanroom facility was determined to be $7.5 \,\mu$ m.

The total resistance of the Graphite sample and the entire circuit resistance were measured using 2400 source meter and 2182 nanovoltmeter, and determined at 0.01224 Ω and 0.116 Ω respectively. The resistivity of the graphite was calculated by the following:

$$\rho_{graphite} = R_{graphite} \frac{A_{cross-sectional}}{lenth}$$
$$= 0.01224\Omega \frac{(0.618cm)(0.633cm)}{5.09cm}$$
$$= 9.41 \times 10^{-4} \Omega cm$$

This value was compared to the standard graphite resistivity, from the material data sheet [53], which is 0.006 Ω cm. However, we measured a resistivity of approximately 0.001 Ω cm. The difference between these values might come from the differences in processing of the two graphite samples. The sample measured during this experiment was denser than the standard graphite, and thus its resistivity is lower.

In the case of the graphite sample, the oscillator was again set at the 1 V rms and 150 Hz for output voltage and frequency respectively. Initially, a high frequency on the order of 100k Hz, was used to achieve stable data, however, the high frequency measurement was not as stable as the one at 150 Hz. The current measured by 1 Ω resistor is: 19.59 mA. And the circuit analysis for this sample is shown bellow: The voltage drop, across the entire circuit, measured by the lock-in amplifier is: 3.62mV Adding this to the voltage drop across the resistor box: 19.59mV + 3.62mV = 23.21 mV The voltage across internal impedance of lock-in is: 1V (rms oscillating output voltage) – 23.21mV = 0.9768 V.

Thus the internal impedance is: $\frac{0.9768V}{19.59mA} = 49.86\Omega \cong 50\Omega$.

Thus the internal resistance value was verified for this case as well.

The data taken by one probe scanning conductivity measurement system using Pt microelectrode is tabulated (Table 6.4) and plotted (Figure 6.17) in the following:

Probe spacing	Voltage difference
0 cm	2.36 mV
.1 cm	2.37 mV
.2 cm	2.37 mV
.3 cm	2.38 mV
.4 cm	2.38 mV
.5 cm	2.38 mV
.6 cm	2.39 mV
.7 cm	2.39 mV
.8 cm	2.40 mV
.9 cm	2.40 mV
1.0 cm	2.40 mV
1.1 cm	2.41 mV
1.2 cm	2.41 mV
1.3 cm	2.41 mV
1.4 cm	2.43 mV
1.5 cm	2.43 mV
1.6 cm	2.44 mV
1.7 cm	2.44 mV
1.8 cm	2.45 mV
1.9 cm	2.46 mV
2.0 cm	2.46 mV
2.1 cm	2.46 mV
2.2 cm	2.47 mV
2.3 cm	2.47 mV
2.4 cm	2.47 mV
2.5 cm	2.48 mV
2.6 cm	2.49 mV

Table 6.4 Data of scanned voltage difference of graphite using AC technique and Pt microelectrode.



Figure 6.17 Plot of scanned voltage difference of graphite using AC technique and Pt microelectrode.

The linear fit to the data in Figure 6.17 gives a slope of 0.048596 (mV/cm). Thus resistivity is:

$$\rho = R \frac{A}{l} = \frac{\Delta VA}{I\Delta l}$$

= $\frac{(0.048596mV / cm)(.618cm)(.633cm)}{(19.59mA)}$
= $9.7004 \times 10^{-4} \Omega cm$

This result with the lock-in amplifier is very close to the resistivity value determined by four-point probe method ($\rho = 9.41 \times 10^{-4} \Omega cm$). The electrical conductivity of the graphite sample is simply the reciprocal of resistivity: $\sigma_{\text{graphite}} = 1031$ S/cm.

6.3.5 Bi₂Te₃

Although Bi_2Te_3 sample was measured by DC conductivity measurement technique, the data analysis with its calculation was not ultimate. The voltage difference should always increase strictly with a probe spacing; however, it decreased occasionally. It is speculated that the decrease was due to the topographical problem such as cracks in the sample and the surface oxidation. Although the sample surface was treated by scraping using razor blade, the crack in sample is sometimes genuine and could not be treated by the surface treatment. The expected range of the electrical conductivity of Bi_2Te_3 sample is about 800S/cm to 1200 S/cm; however, with the DC analysis the average of the conductivity was achieved at 702 S/cm.

In order to inspect the problem, the measurement of Bi_2Te_3 sample was revisited with AC conductivity measurement technique using lock-in amplifier. First to verify the samples topographical problem, the same kind of sample of Bi_2Te_3 , in which the crack exists as the sample measured in DC technique, was used. The new good sample of Bi_2Te_3 is then characterized consecutively to test the Pt microprobe capabilities.

In the case of the Bi₂Te₃ sample, the lock-in amplifier was set to 0.5 V rms, 1 kHz as the oscillator output signal values. The amplitude of the voltage was decreased to source the current approximately equal to the one used for DC measurement: 10mA. The current of the system was calculated by measuring voltage difference across the 1 Ω resistance: I = 9.002 mA. The output frequency was chosen by running a frequency sweep. The start frequency and the stop frequency was chosen as 1 Hz and 10 kHz respectively. Thus, the frequency was swept linearly from 1 Hz to 10 kHz with the step frequency of 100 Hz, and the optimizing frequency was observed by the stability plot. Around 1 kHz, the input signal became stable, and thus, 1 kHz was selected as the output frequency. Also, in order to see the micro range of the input voltage data, the input sensitivity on the lock-in amplifier was decreased to 5 mV from 100 mV. The Bi₂Te₃ sample was run three times, and the data (Table 6.5) and plot (Figure 6.19) are in the following.

Probe spacing	Voltage difference	Voltage difference	Voltage difference
(cm)	1 st run (mV)	2 nd run (mV)	3 rd run (mV)
0.000 cm	2.821 mV	4.110 mV	3.867 mV
0.025 cm	2.681 mV	4.140 mV	3.894 mV
0.050 cm	2.858 mV	4.128 mV	3.909 mV
0.075 cm	2.759 mV	4.116 mV	3.915 mV
0.100 cm	2.787 mV	4.116 mV	3.916 mV
0.125 cm	2.904 mV	4.112 mV	3.889 mV
0.150 cm	2.901 mV	4.114 mV	3.910 mV
0.175 cm	2.976 mV	4.112 mV	3.920 mV
0.200 cm	3.050 mV	4.120 mV	3.927 mV
0.225 cm	3.150 mV	4.122 mV	3.929 mV
0.250 cm	3.057 mV	4.120 mV	3.932 mV
0.275 cm	3.040 mV	4.130 mV	3.937 mV
0.300 cm	3.051 mV	4.130 mV	3.941 mV
0.325 cm	3.120 mV	4.132 mV	3.948 mV
0.350 cm	3.204 mV	3.940 mV	3.953 mV
0.375 cm	3.235 mV	4.143 mV	3.958 mV
0.400 cm	3.222 mV	4.150 mV	3.962 mV
0.425 cm	3.245 mV	4.155 mV	3.968 mV
0.450 cm	3.250 mV	4.151 mV	3.968 mV
0.475 cm	3.255 mV	4.153 mV	3.972 mV
0.500 cm	3.260 mV	4.154 mV	3.975 mV
0.525 cm	3.263 mV	4.146 mV	3.976 mV
0.550 cm	3.268 mV	4.136 mV	3.989 mV
0.575 cm	3.271 mV	4.143 mV	4.000 mV
0.600 cm	3.275 mV	4.136 mV	3.988 mV
0.625 cm	3.277 mV	4.141 mV	4.003 mV
0.650 cm	3.276 mV	4.174 mV	4.012 mV
0.675 cm	3.277 mV	4.180 mV	3.821 mV
0.700 cm	3.282 mV	4.185 mV	4.025 mV

Table 6.5 Data of scanned voltage difference of Bi₂Te₃ using AC technique and pin.

In the case of the 2^{nd} run data, the voltage difference decreased abruptly when the probe spacing moved from 0.325 cm to 0.350 cm. The probe was again brought back to the l = 0.325 cm location to see if this is the sudden offset or the topographical problem. The voltage increase was seen at 0.325 cm, and thus it proves that the abrupt decrease was due to cracks or surface contaminants on the sample. Also those three data sets were

scanned different location in width (Figure 6.18), and thus the data jump at different l for each run, supporting the hypothesis that surface cracks exist.



Figure 6.18 Scanning location of each run



Figure 6.19 Plot of scanned voltage difference of Bi₂Te₃ using AC technique and pin.

Since slope of the plot is $\Delta V / \Delta l$

$$\sigma = \frac{I\Delta l}{\Delta VA}$$
$$= \frac{I}{slope \times A}$$

The dimensions of this Bi_2Te_3 sample are: width = 3.41 mm, thickness = 2.25 mm, and length = 9.02 mm.

$$\sigma_{1} = \frac{9.002mA}{(0.16018mV/cm)(0.341cm \times 0.225cm)} = 732S/cm$$

$$\sigma_{2} = \frac{9.002mA}{(0.07683mV/cm)(0.341cm \times 0.225cm)} = 1527S/cm$$

$$\sigma_{3} = \frac{9.002mA}{(0.13797mV/cm)(0.341cm \times 0.225cm)} = 850S/cm$$

$$\sigma_{average} = \frac{\sigma_{1} + \sigma_{2} + \sigma_{3}}{3} = 1036S/cm$$

Conductivity measurement on the 1st run clearly exhibited noise over the first 3 mm of the sample scanned. To investigate the influence of contact resistance, at the correct leads, on the measurements, the input mode was changed from single node A measurement (A-Ground) to the differential measurement (A-B). In this way, the input voltage can be measured strictly between node A and B. The node A was connected to the V+ scanning probe as it used to be; however, the input node B was connected to the I-side of the sample. A copper wire (diameter = 50 μ m) was silver pasted to I- side of the sample, and it was connect to the BNC cable for input node B (Figure 6.20). Using differential measurement the voltage difference across the I- copper wiring was neglected. The input impedance of the lock-in amplifier is 1M Ω and thus the resistance of the copper wire (diameter = 50 μ m) connected to BNC cable was neglected. In this way, the pure voltage difference of the Bi₂Te₃ sample can be measured. In this new configuration

the voltage difference did not decrease as much as we expected, however, the stability on the datasets of 2^{nd} and 3^{rd} run was tremendously improved after the change to the differential measurement on the lock-in amplifier.



Figure 6.20 Setup of the differential voltage measurement.

• New Bi₂Te₃ sample

After verifying the topographical problem of some Bi_2Te_3 sample, a new Bi_2Te_3 was acquired for the next measurement. Again the lock in amplifier was set to 0.5 V rms, 1 kHz as the oscillator output signal values. The current of the system was measured at 9.76 mA. In order to decrease the contact resistance of the silver paste, the small amount of the silver paste was applied under the microscope to make a connection of I+ and I-. And also the copper wire is now pasted on the top surface of the Bi_2Te_3 sample (Figure 6.21).



Figure 6.21 The set up of differential voltage measurement connecting node B on the top surface.

For this new sample, the ends of the sample were nickel plated before making the silver paste contacts for the I+ and I- contacts. Thus the silver paste is pasted on to the thin layer of the nickel layer for the connection of I- and I+.

With these efforts, the voltage difference on the initial probe location decreased to approximately 42 μ V. The scanned voltage of this new Bi₂Te₃ sample is tabulated (Table 6.6) and plotted (Figure 6.22).

Probe spacing	Voltage difference	Voltage difference	Voltage difference			
	(1 st run)	(2 nd run)	(3 rd run)			
0.000 cm	0.042 mV	0.048 mV	0.049 mV			
0.025 cm	0.045 mV	0.051 mV	0.051 mV			
0.050 cm	0.048 mV	0.053 mV	0.053 mV			
0.750 cm	0.049 mV	0.055 mV	0.055 mV			
0.100 cm	0.052 mV	0.058 mV	0.058 mV			
0.125 cm	0.055 mV	0.060 mV	0.060 mV			
0.150 cm	0.058 mV	0.062 mV	0.063 mV			
0.175 cm	0.059 mV	0.064 mV	0.065 mV			
0.200 cm	0.061 mV	0.068 mV	0.068 mV			
0.225 cm	0.066 mV	0.070 mV	0.069 mV			
0.250 cm	0.070 mV	0.072 mV	0.073 mV			
0.275 cm	0.072 mV	0.075 mV	0.075 mV			
0.300 cm	0.073 mV					
0.325 cm	0.074 mV					

Table 6.6 Data of scanned voltage difference of new Bi₂Te₃ using AC technique and pin probe.



Figure 6.22 Plot of scanned voltage difference of new Bi₂Te₃ using AC technique and pin probe.

The voltage difference linearly increased with slopes indicated in Figure 6.22. The dimensions of the Bi₂Te₃ were: w = 4.45 mm, t = 2.31 mm, and L = 4.45 mm. The electrical conductivity was then calculated in each run as follows.

$$\sigma_{1} = \frac{(9.76mA)}{(0.10338mV/cm)(0.445cm)(0.231cm)} = 918S/cm$$

$$\sigma_{2} = \frac{(9.76mA)}{(0.096504mV/cm)(0.445cm)(0.231cm)} = 984S/cm$$

$$\sigma_{3} = \frac{(9.76mA)}{(0.095804mV/cm)(0.445cm)(0.231cm)} = 991S/cm$$

$$\sigma_{average} = \frac{918 + 984 + 991}{3} = 964S/cm$$

As mentioned earlier the range of the electrical conductivity of the Bi_2Te_3 sample is about 800S/cm to 1200 S/cm, and thus the result achieved here met the criteria successfully. Here in order to estimate the contact resistance from silver paste, the node B was again brought back to the I- side of the Bi_2Te_3 sample. The scanned voltage including contact resistant is tabulated (Table 6.7) and plotted (Figure 6.23) in the following.

Probe spacing (cm)	Voltage difference (mV)
0.000 cm	0.013 mV
0.025 cm	0.042 mV
0.050 cm	0.044 mV
0.075 cm	0.046 mV
0.100 cm	0.048 mV
0.125 cm	0.050 mV
0.150 cm	0.052 mV
0.175 cm	0.054 mV
0.200 cm	0.056 mV
0.225 cm	0.059 mV
0.250 cm	0.061 mV
0.275 cm	0.063 mV
0.300 cm	0.065 mV
0.325 cm	0.068 mV
0.350 cm	0.070 mV
0.375 cm	0.073 mV
0.400 cm	0.075 mV
0.425 cm	0.077 mV
0.450 cm	0.080 mV
0.475 cm	0.082 mV
0.500 cm	0.098 mV

 Table 6.7
 Data of scanned voltage difference of new Bi₂Te₃ using AC technique and pin probe for contact resistance analysis.

The contact resistance of the silver paste is calculated as follows.

$$\sigma_{contact R} = \frac{(0.042 - 0.013)mV}{9.76mA} = 1.23 \ m\Omega$$

$$\sigma_{contact R} = \frac{(0.098 - 0.082)mV}{9.76mA} = 1.64 \ m\Omega$$





Figure 6.23 Plot of scanned voltage difference of new Bi₂Te₃ using AC technique and pin probe for contact resistance analysis.

0.1

0.08

0.06

0.04

0.02

Voltage difference (mV)

To see the voltage difference due to the contact resistance from the silver paste, the probe was placed at the sides of the sample where the silver paste was coated. Thus the rapid increase of voltage difference at the both ends (l=0.025 cm and l=0.500cm) was due to the contact resistance created between the sample and the silver paste.

Only the linear region of the scanned voltage fit to determine the slope of 0.089684 mV/cm, thus the electrical conductivity was calculated as follows:

$$\sigma = \frac{(9.76mA)}{(0.08968mV / cm)(0.445cm)(0.231cm)} = 1059S / cm$$

Now, after the verification of the good Bi_2Te_3 sample including the setting up of the AC conductivity measurement system, the Pt microprobe (7.5 µm diameter) was employed to the system to explore the feasibility of it. The scanned voltage difference measured using Pt microprobe is tabulated (Table 6.8) and plotted (Figure 6.24) in the following.

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Probe spacing (cm)	Voltage difference (mV)				
0.000 cm	0.050 mV				
0.025 cm	0.051 mV				
0.050 cm	0.052 mV				
0.750 cm	0.055 mV				
0.100 cm	0.057 mV				
0.125 cm	0.059 mV				
0.150 cm	0.061 mV				
0.175 cm	0.063 mV				
0.200 cm	0.064 mV				
0.225 cm	0.065 mV				
0.250 cm	0.069 mV				
0.275 cm	0.071 mV				
0.300 cm	0.075 mV				
0.325 cm	0.075 mV				
0.350 cm	0.079 mV				
0.375 cm	0.082 mV				
0.400 cm	0.084 mV				
0.425 cm	0.086 mV				
0.450 cm	0.099 mV				

Table 6.8	Data of scanned voltage difference of new Bi ₂ Te ₃ using AC
	technique and Pt microprobe.

The sudden voltage increase at the location 0.45 cm is due to the contact resistance of nickel plating estimated as 922 $\mu\Omega$.

 $R_{contact}_{resistance} = \frac{0.095(mV) - 0.086(mV)}{9.76(mA)} = 0.922m\Omega$

The Nickel plating of the I+ side was observed little thicker than the I- side under the microscope, and thus the Pt microprobe could detect the contact resistance of the nickel plating here. The Pt microprobe scanned strictly on the top surface of the Bi_2Te_3 sample, so this voltage increase due to the contact resistance is purely from Nickel plating.



Figure 6.24 Plot of scanned voltage difference of new Bi₂Te₃ using AC technique and Pt microprobe.

The conductivity of the Bi_2Te_3 sample was measured using Pt microprobe and calculated as follows:

$$\sigma = \frac{(9.76mA)}{(0.086852mV / cm)(0.445cm)(0.231cm)} = 1093S / cm$$

This is a reasonable result in good agreement with our previous measurements and published values for Bi_2Te_3 .

6.4 Data acquisition Instrumentation

This section describes the specification of the instruments used to acquire the electrical conductivity measurement.

6.4.1 Keithley Model 2400 SourceMeter®

The Model 2400 SourceMeter combines a precise, low-noise, highly stable DC power supply with a low noise, highly repeatable, high-impedance multi-meter which incorporates the following features:

- 0.012% basic measurement accuracy, 0.035% basic source accuracy with 5-1/2 digit resolution. 1000 readings/second at 4-1/2 digits via GPIB.
- Voltage source/measure range: $\pm 1\mu V \sim \pm 200V DC$.
- Current source/measure range: ± 10pA ~ ± 1A. Concurrent measurements of all three functions over the remote interface.
- Source-measure sweep capabilities (linear and logarithmic staircase sweeps).
- 22W, 4-quadrant source and sink operation.
- Trigger-link interface to Keithley series 7000 switching hardware.
- IEEE-488 and RS 232 interfaces.

This model 2400 SourceMeter was used to source current to the sample measured for electrical conductivity.

6.4.2 Model 2182 Keithley Nanovoltmeter

- Dual channels for measuring voltage and temperature.
- Synchronization to line
- Direct reading of ratio
- Low noise at high speeds

6.4.3 EG&G 7265 DSP (Digital Signal Processor) Lock-In Amplifier

The EG&G lock-in amplifier has been employed to perform AC electrical conductivity measurement for the noise improvement, with the following features:

- Oscillator frequency range: 0.001 Hz ~ 250 kHz with absolute accuracy 225 ppm ± 30 μHz.
- Amplitude range: $1 \mu V \sim 5 V$ with $1 \mu V \sim 1.25$ mV resolution.
- Signal channel voltage sensitivity: 2 nV ~ 1 V full-scale
- Current input mode sensitivities: 2 fA to 1μ A full-scale
- Line frequency rejection filter
- Dual phase demodulator with X-Y and R- θ outputs
- Very low phase noise of < 0.0001° rms.
- Output time constant: $10 \ \mu s \sim 100 \ ks$.
- Output oscillator impedance: 50Ω
- Signal reference mode AC gain limit: 90 dB

- Auto-phase: In an Auto-Phase operation the value of the signal phase is computed and an appropriate phase-shift is then introduced into the reference channel. So the measured signal phase shift is zero to input signal.

7. CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

7.1 One point probe scanning conductivity measurement system.

A new scanning probe electrical conductivity measurement system was designed, implemented, and tested. The system is based on nanoprobes with tip dimensions of 300 nm ~ that were fabricated using a CO₂ laser based micropipette puller. Pulled nanoelectrodes containing different types of metals (e.g. gold and Pt) were tested successfully in the scanning probe electrical conductivity measurement system. The measurement system was tested for both ac and dc electrical conductivity measurements. The electrical conductivity of the semiconductor compound Bi_2Te_3 , a copper strip, and a graphite sample were measured by the system. With this electrode probe, the force created while making contact is significantly reduced. Thus, it can be used for extremely fragile samples such as small single crystals of new materials.

7.2 Suggestions for Future work

7.2.1 Heat treatment

For one application of the pulled pipette, a quartz pulled pipette without any metal filament was sputter coated with gold on the outside surface to make a nanoelectrode. It was found that with this nanoelectrode it was difficult to make good electrical contact to the sample. It is speculated that the difficulty in making contact is due to the several reasons:

- The sample surface has problems caused by topographical variations or oxidation.
- The gold coating did not adhere well to the quartz, and was removed at the point of contact.

In order to mitigate the second problem, the nanoelectrode was annealed at the appropriate temperature to improve adhesion. Another alternative is to introduce an intermediate layer such as chromium between the glass and the gold material, and followed this with the heat treatment. This requires a good thin film deposition system including multiple shutters for coating different metals consecutively.

7.2.2 Study of a compound semiconductor with the domain including doping profile

Often new compound semiconductor samples contain domains in which the electrical conductivity is different can vary. It is common that these domains will be on the order of 10-100 μ m in dimension. Some of the domains have doping profiles / striation within the domain with 40 nm spacing. In these samples it is speculated that the spontaneous formation of these striations is key to improving the material properties of interest for thermoelectric materials. In order to characterize such domains, probes with tip dimensions smaller than 10 μ m are essential. The nanoelectrodes fabricated in our lab have tip dimensions less than 300 nm, and thus are well suited to studying the characteristics of these domains and gaining insight into the further development of the

thermoelectric materials here at MSU. The nanoelectrode was successfully fabricated and tested with different semiconductor compounds and metals. This probe could be used to provide information about the electrical characteristics of each domain including their doping profiles.



Figure 7.1 Doping profile/ striation

7.2.3 Pulled pipette as a thermocouple

Using P-2000 micropipette puller, thermocouples can be designed very easily. First, pull the micropipette with metal, and then the outside of the probe can be coated with another type of metal. This would allow for a localized temperature measurement probe that could simultaneously be used for measuring the voltage at the point of contact. With the addition of a separate localized heating source, then thermoelectric power measurements could be made on a local scale. With such probes, doping profiles could be imaged by scanning over the surface of a sample.

APPENDIX

8. APPENDIX

• The pulling program code on P-2000 micropipette puller

Selection A)	Gold wire	$(d = 50 \mu m),$	Borosilicate gl	lass (o.d.=1.0	mm, i.d.= 0.5mm)

	Heat	Filament	Velocity	Delay	Pull	Comment
Step 1	400	4	50	200	20	2 pulls
Step 2	355	4	40	0	65	Final pull

Selection B) Platinum wire $(d = 50\mu m)_{t}$ Quartz glass (o.d.=1.0mm, i.d.=0.5mm)

	Heat	Filament	Velocity	Delay	Pull	Comment
Step 1	625	8	50	200	65	2 pulls
Step 2	645	2	80	0	75	Final pull
BIBLIOGRAPHY

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9. **BIBLIOGRAPHY**

- 1. http://www.melcor.com/history.htm
- 2. D.M. Rowe, <u>CRC Handbook of Thermoelectrics</u>, CRC Press, New York, 1994.
- 3. http://www.sutter.com/
- 4. Munoz, J.L. and Coles, J. "Quartz micropipettes for intracellular voltage microelectrodes and ion selective microelectrodes," *Journal of Neuroscience Methods*, 22:57-64, 1987.
- 5. F.M. Smits, Bell Sys. Tech. J., May (1958).
- 6. P. Boggild and T.M. Hansen, "Scanning Nanoscale Multiprobes for Conductivity Measurements", *Review of Scientific Instruments*, Vol. 71, No. 7, pp. 2781-2783, July 2000.
- 7. http://mitghmr.spd.louisville.edu/sops/sop45.html
- 8. S.M.Sze, <u>VLSI Technology</u>, 2nd edition, New York: pp 32, 1988.
- 9. http://microlab.berkeley.edu/~ee143/Four-Point_Probe/
- 10. S.M.Sze, <u>VLSI Technology</u>, 2nd edition, New York: pp300, 1988.
- 11. Bhagwan D. Agarwal, <u>Analysis and Performance of Fiber Composites</u>, Wiley, New York, 1980.
- 12. Arges, K. Pete., Mechanics of Materials, New York, McGraw-Hill, 1963.
- Best Charles L., <u>Analytical Mechanics for Engineers Statics</u>, Scranton, International Textbook Co., 1965.
- 14. G. Fish, "Ultrafast response micropipette-based submicrometer thermocouple", *Rev. Sci. Instrum.*, 66 (5), May 1995.
- 15. Rimma Dekhter, A.Lewis, "Investigating material and functional properties of static random access memories using cantilevered glass multiple-wire force-sensing thermal probes", *Applied Physics Letters*, Vol. 77, No. 26, pp 4425-4427, December 2000.

- 16. A. Lewis, M. Isaacson, A. Hartoonian, and A. Murray, "Scanning optical spectral microscopy with 500 Å spatial resolution", *Biophys. J.*, p.405a, 1983.
- 17. http://www.jasco.co.uk/nearfield.htm
- Alina Strinkovski, "Chemical Application of Near-Field Scanning Optical Microscopy: Surface and Near-Surface Chemical Imaging with Conventional Near-Field Optical Probes and Externally Illuminated Chemically Active Ion Sensors", *Israel Journal of Chemistry*, Vol. 41, pp.129-137, 2001.
- 19. Hartoonian, A., Shambrot, E., Radko, A., Lieberman, K., Ezekiel, S., Veinger, D., Yampolski, G., Proc. IEEE, 88, pg. 1471, 2000.
- 20. Shmuel Shalom, "A micropipette force probe suitable for near-field scanning optical microscopy", *Rev. Sci. Instrum.*, 63 (9), September 1992.
- 21. A. Lewis and K.Lieberman, Nature, 354, pg 214, 1991.
- 22. Shmuel Shalom, "A micropipette force probe suitable for near-field scanning optical microscopy", *Rev. Sci. Instrum.*, 63 (9), September 1992.
- 23. G. Meyer and N. Amer, Appl. Phys. Lett., 53, pg. 1045, 1988.
- 24. Mun-Heon Hong, Ki Hyun Kim, "Scanning nanolithography using a material filled nanopipette", *Applied Physics Letters*, Vol. 77, No. 16, pg 2605, 2000.
- 25. A.D. Muller and F. Muller, "Resonance frequency shift caused by the friction of a drop of water in air: An approach to estimate shear forces in scanning probe microscopies", *Applied Physics Letters*, Vol. 78, No. 14, April 2001.
- 26. J. O. Tegenfeldt and L. Montelius, Appl. Phys.Lett., 66, pp 1068, 1995.
- 27. C. L. Petersen, F. Grey, M. Ono, Surf. Sci., 377-379, 676, 1997.
- 28. P.L McEuen, N. G. Chopra, A. Zettl, A. Thess, R. E. Smalley, *Science*, Vol. 275, pg. 1922, 1997.
- Peter Boggild, Rancois Grey, Tue Hassenkam, Daniel R. Greve, and Thomas Bjornholm, "Direct Measurement of the Microscale Conductivity of Conjugated Polymer monolayers", Advanced Materials, Vol. 12, no.13, pp. 947-950, July 5th 2000.

- C.L. Petersen, T.M Hansen, P.Boggild, A. Boisen, O. Hansen, T. Hassenkam, F. Grey, "Scanning microscopic four-point conductivity probes", Sensors and Actuator A. 96 (2002) 53-58.
- P. Boggild, T.M. Hansen, O.Kuhn, and F. Grey, "Scanning nanoscale multiprobe for conductivity measurements", *Review of Scientific Instruments*, Vol. 71, No.7, pp. 2781-2783, July 2000.
- 32. T.Fujii et al., J. Vac. Sci. Technol. B, Vol. 9, pg. 666, 1991.
- 33. T. Junno, S. B. Carlsson, H. Xu, L. Montelius, and L. Samuelson, Appl. Phys. Lett., Vol. 72, pg. 548, 1998.
- 34. M. Wendel, H. Lorenz, and J. P. Kotthaus, Appl. Phys. Lett., Vol. 67, pg. 3732, 1995.
- 35. M. Wendel, B. Irmer, J. Cortes, R. Kaiser, H. Lorenz, J.P. Kotthaus, A. Lorke, and E. Williams, *Superlattices Microstruc.*, Vol. 20, pg. 349, 1996.
- 36. Kim P and Lieber CM 1999 Science 386 2148
- 37. http://www.metals.com
- 38. G. Fish and O. Bouevitch, Ultrafast response micropipette-based submicrometer thermocouple, Rev. Sci Instrum. Vol 66, No.5, May 1995.
- 39. Sutter Instrument Company, P-2000 micropipette puller operation manual
- 40. Stephen A. Campbell, <u>The Science and Engineering of Microelectronic Fabrication</u>, Oxford University Press, New York, pg 70, 1996.
- 41. Stephen A. Campbell, <u>The Science and Engineering of Microelectronic Fabrication</u>, Oxford University press, New York, pg 72, 1996.
- 42. Etching profiles: http://www.ee.washington.edu/class/539/Lectures/lecture2/sld020.htm
- 43. Werner Kern, and Cheryl A. Deckert, <u>Thin film processes- Chemical Etching</u>, Academic Press. Inc. pp 443, 1978.
- 44. Varian, "Product Catalog 2000", Varian Vacuum Products. Inc. pg 579, 2000
- 45. David R. Lide, <u>Handbook of Chemistry and Physics 79th edition</u>, CRC Press, pg.12-191-192, 1999.

- 46. <u>http://www.bridgetec.com/janhall.html</u> (June, 2001)
- 47. Keithley Instruments, "Model 2400 SourceMeter User's Manual", Fifth Printing, June 1998.
- 48. K.N.Subramanian, and T.P.Hogan, "Internal Damage Accumulation Resulting from Thermomechanical Fatigue in Lead-Free Solder Joints", a proposal submitted to National Science Foundation, p.7, November 2002.
- 49. Keithley Instruments, "Model 2182 Nanovoltmeter User's Manual", Second Printing, June 1998.
- 50. PerkinElmer Instruments, "What is a lock-in Amplifier?", Technical Note TN1000, 2000.
- 51. EG&G Instruments, "Model 7265 DSP Lock-in Amplifier Instruction Manual", 1998.
- 52. David R. Lide, "CRC Handbook of Chemistry and Physics", 79th edition 1998-1999.
- 53. <u>http://www.matls.com</u> (August, 2002)

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