Basic 10
Micro-Nano Materials Characterization and Inspection
- Evaluation of Electrical Properties-

Prof. Yang Ju

Dept. of Mechanical Science and Engineering

Nagoya University, Japan

Outline

1. The recent researches

2. Four-point probe method

3. Four-point AFM probe method

4. Microwave AFM method

1. The recent researches

Evaluation of electrical properties of metallic nanomateirals

2. Four-point probe method

3. Four-point AFM probe method

4. Microwave AFM method

Introduction

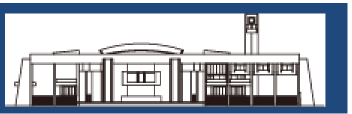
Nanomaterials

- Low-dimensional materials whose crystal structures arrange in zero-dimensional dot, one-dimensional chain or two-dimensional plane, such as nanoparticle, nanowire, nanowhisker, nanorod, nanobelt, nanotube and nanofilm

One-dimensional (1D) metallic nanostructures

- The display of a plethora of electrical, optical, chemical and magnetic properties with diverse applications
- The important role in semiconductor industry or integrated circuit (IC) of metallic nanowires

The evaluation of electrical conductivity (resistivity) of 1D metallic nanomaterials, especially metallic nanowires



Introduction

Size-dependent of the electrical properties such as conductivity of metallic materials

- The electrical resistivity of metallic nanomaterials increases once the dimensions decrease below the bulk electronic mean free path.
- Grain boundary scattering and surface scattering are recognized to be two most important mechanisms for size-dependent conductivity of metallic nano-conductors at room temperature.
- Electron-electron interactions, localization, and electron-phonon interactions known as intrinsic contributions can also influence the conductivity of metallic nanomaterials, especially at extremely low temperature.

Quantized effects in metallic nanowires and thin films are significant only for dimensions approaching Fermi wavelength of materials (a few nanometers), and they are not presently of practical concern.

Conductivity measurement of metallic nanowires

To study the temperature- and size-dependent resistivity of metallic nanowires, many experimental measurements have been carried out since the beginning of 1980s.

Resistivity of metallic nanowires

$$\rho = R \cdot \frac{A}{l}$$

R: measured resistance
A: cross section area of the nanowire
l: length of the nanowire

The values which should be measured directly include the geometry, dimensions of the nanowires, as well as the resistance of a single nanowire or several parallel and non-contact nanowires.

Geometry (cross-section shape) of nanowires

Four kinds of fabrications of the metallic nanowires used for resistivity measurement

1. Nanowires deposited into pores of porous membrane templates including polycarbonate membranes(1)-(3) and anodic alumina membranes(4)
   - Fabricated nanowires can be free-standing ones mainly with circular cross-sections which are preferred for their regularity.
2. Metallic nanowires deposited in the pre-manufactured trenches on substrates(5)-(7)
   - The trenches can be made by lithography or so-called spacer technique.
   - The cross-sections of fabicated nanowires are always trapezoidal and rectangular.

(1) Liu K et.al., (1998) Phys Rev B 58:14681-14684, (2) Toimil-Molares ME et.al., (2003) Appl Phys Lett 82:2139-2141, (3) Bid A et.al.(2006) Phys Rev B 74:035426(1-8), (4) Zhang ZB et.al., (2000) Phys Rev B 61:4850-4861, (5) Maîtrejean S et.al., (2006) Microelectron Eng 83:2396-2401, (6) Marom H et.al., (2006) Phys Rev B 74:045411(1-9), (7) Zhang W et.al., (2007) J Appl Phys 101:063703(1-11)

Geometry (cross-section shape) of nanowires

3. Nanowires deposited directly onto substrates by evaporation(8) or sputtering(9)
   - The cross-sections are always trapezoidal and difficult to control.
4. The DNA-templated metallic nanowires(10)-(13)
   - Although the cross-sections of these nanowires constructed by metallic particle clusters attached to the DNA templates are always irregular, they were mostly assumed to be circular for convenience.

The observation of cross-sections can be performed by various types of equipments including transmission electron microscope (TEM), scanning tunneling microscope (STM) and atomic force microscope (AFM), as well as scanning electron microscope (SEM).

(8) Huang Q et.al., (2009) Appl Phys Lett 95:103112, (9) Hinode K et.al., (2001) Jpn J Appl Phys, Part 2 40:L1097-L1099 (10) Braun E et.al., (1998) Nature 39:775-778, (11) Richter J et.al., (2001) Appl Phys Lett 78:536-538, (12) Richter J et.al., (2002) Appl Phys A 74:725-728, (13) Keren K et.al., (2002) Science 297:72-75

Measuring the dimensions of nanowires (length and cross-section area)

When the cross-sections cannot be kept constant due to fabrication technologies, the average cross-section areas also can be estimated by calibration measurements(9),(14),(15).

The average cross-section area

$$A = \left(\frac{\mathrm{d}\rho}{\mathrm{d}T}\right) \Big/ \left(\frac{\mathrm{d}R}{\mathrm{d}T}\right) \cdot l$$

A: cross section area of the nanowire
l: length of the nanowire
R: measured resistance
ρ: resistivity of the nanowire
T: temperature

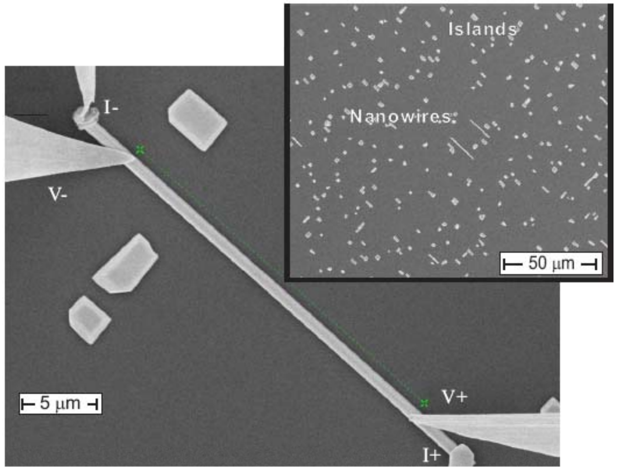
The length of nanowires under testing ranges from several micrometers to hundreds of micrometers, which can be steadily measured by microscopes.

(14) Steinhögl W at.al., (2005) J Appl Phys 97:023706(1-7),
(15) Maîtrejean S et.al., (2006) Microelectron Eng 83:2396-2401

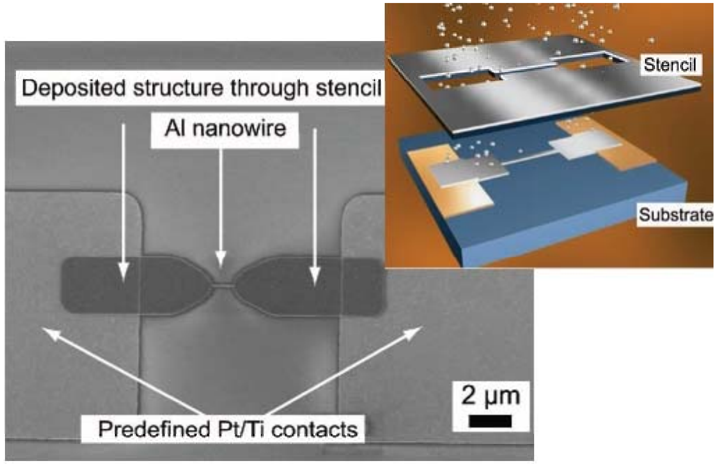
Measuring the resistance of nanowires

Nanowires tested in the same substrate or trench where they are synthesized

- The probes can be connected to the nanowires directly or to electrodes deposited on the nanowires.



The micrograph of silver nanowire under four-point probe measurement (8)*



The micrographs of the microslit stencil-assisted nanowire and electrodes(16)**

(16) Vazquez-Mena O et.al., (2008) Nano Lett 8:3675-3682

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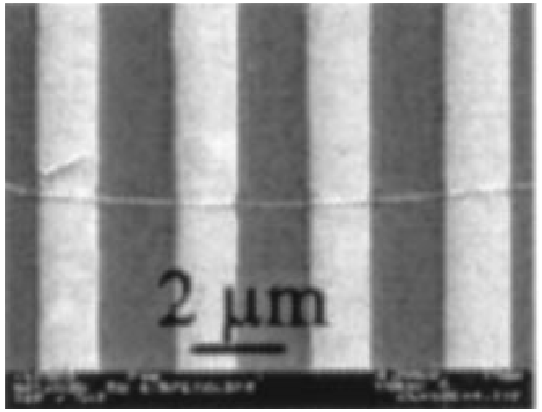
Measuring the resistance of nanowires

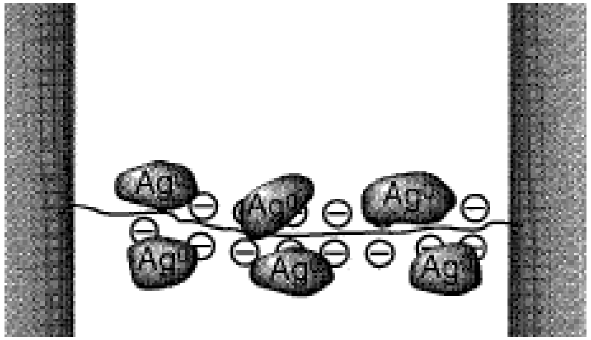
Free-standing nanowires



The micrograph of nanowire connected to four electrodes(2)*

- Some drops of solution containing the wires on a SiO_2 substrate → Creation of four finger-like electrodes on top of the wires
- Deposition of the electrodes → Subsequently place of the wires on top

DNA-templated nanowires



The scheme of assembling DNA-templated metallic nanowire with electrodes(10)**

- The DNA molecules that can be stretched and connected to electrodes by molecular combing before the metallic nanowires were deposited

Determining the grain size of nanowires

In order to quantify the grain boundary scattering, the grain structure of the nanowires should also be determined, which can be done by various microscope and X-ray diffraction method(1),(4),(6),(7),(17),(18).

(17) Durkan C and Welland ME, (2000) Phys Rev B 61:14215-14218
(18) Cornelius TW et.al., (2006) J Appl Phys 100:114307(1-5)

1. The recent researches

2. Four-point probe method

The most common and effective method to measure the resistivity of metallic nanowires

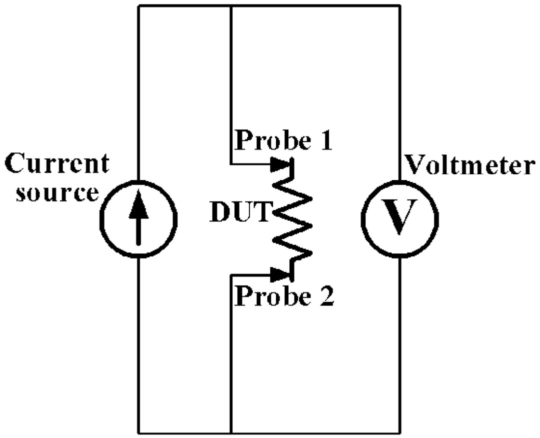
3. Four-point AFM probe method

4. Microwave AFM method

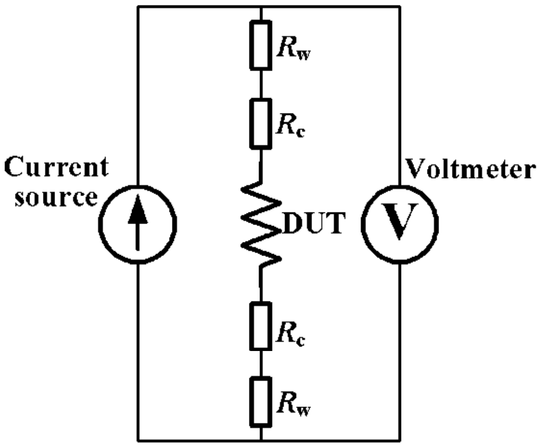
The advantage of four-point probe method

Two-point probe system

- In micro-scale or nano-scale, the contact resistance between device under test (DUT) and the probes always becomes innegligible due to the extremely small contact area.



Sketch of the two-point probe system



Equivalent circuit of the two-point probe system

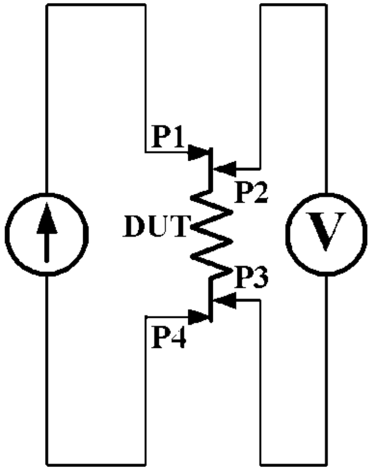
$$R_{\mathrm{m}} = V_{\mathrm{m}} / I = 2R_{\mathrm{c}} + 2R_{\mathrm{w}} + R_{\mathrm{DUT}}$$

V_{m}: Indication of the voltmeter
R_{m}: Measured resitance
R_{c}: Contact resistance
R_{w}: Wire resistance
R_{DUT}: Resistance of DUT

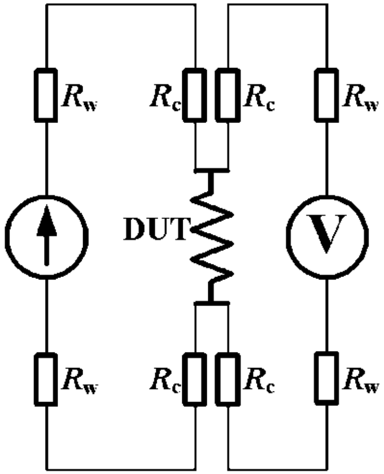
The advantage of four-point probe method

Four-point probe (FPP) system

- FPP method has become very popular since it was introduced by William Thomson (Lord Kelvin), who invented the Kelvin bridge in 1861 to measure very small resistances.



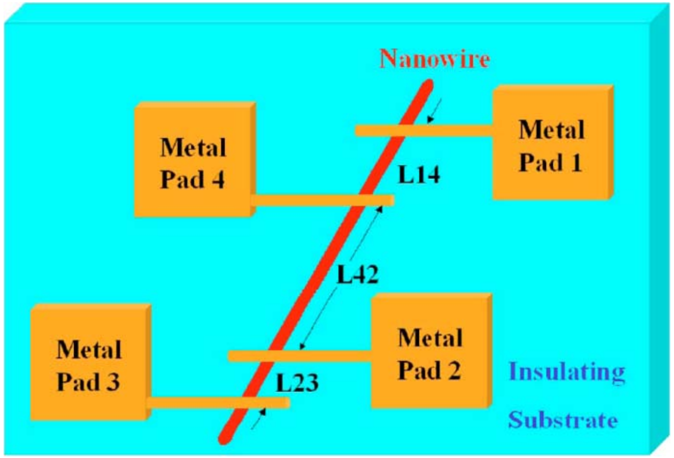
Sketch of the four-point probe system



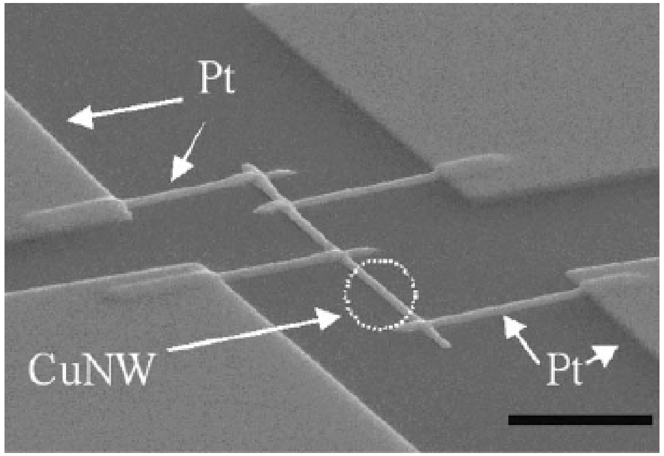
Equivalent circuit of the four-point probe system

- The DUT resistance R_{DUT} can be derived directly by dividing the voltmeter indication V_m by the current indication I in a single measurement.

Modified four-point probe method



Sketch of the modified FPP system (19)*



Micrograph of the modified FPP system(19)*

- The typical current-voltage (*I*-*V*) measurements between each and every pair of pads
- Repeated measurements at each applied voltage with the polarities of the electrodes in the given pair switched for all probing paths
- Derivation of the exact resistance of the nanowire from the measured results

(19) Gu W et.al., (2006) Appl Phys Lett 89:253102(1-3)

1. The recent researches

2. Four-point probe method

3. Four-point AFM probe method

Combination with the conventional four-point probe method and the atomic force microscope thereby providing a capability to characterize the local resistivity of metallic nanowires

4. Microwave AFM method

Four-point AFM probe method

One of the most important issues…

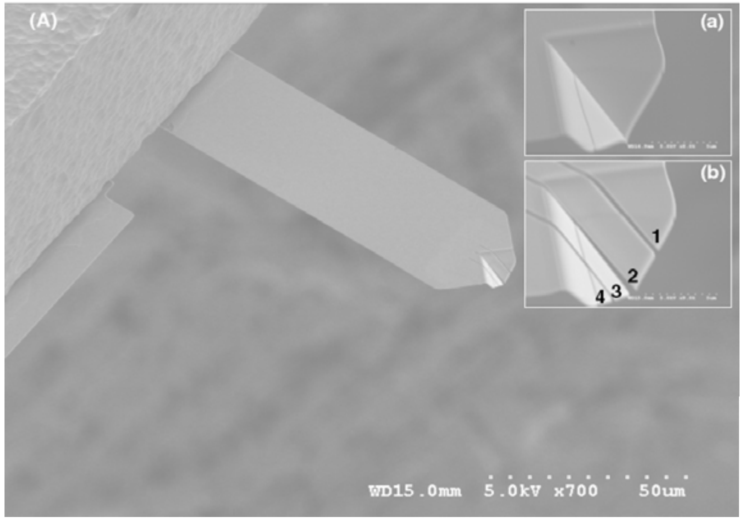
The ambiguous electrical conductivity inside nanowires, with the consequence that nanocircuits and nanodevices do not, usually, function as expected.

A four-point AFM probe technique(20), (21)

- The probe not only retains the ability of surface profile imaging but is also capable of characterizing local conductivity simultaneously.
- The probes can have an electrode spacing as small as several hundreds nanometers and work at AFM contact mode.
- The average force applied to the surface is smaller than 10 pN, which provides a nondestructive measurement and still ensures good electrical conduction between probe and sample.
- The influence of the contact resistance between the electrodes and the sample can be eliminated.

(20) Ju Y et.al., (2005) Rev Sci Instrum 76:086101(1-3)
(21) Ju BF et.al., (2007) J Phys D: Appl Phys 40:7467-7470

Fabrication of four-point AFM probe



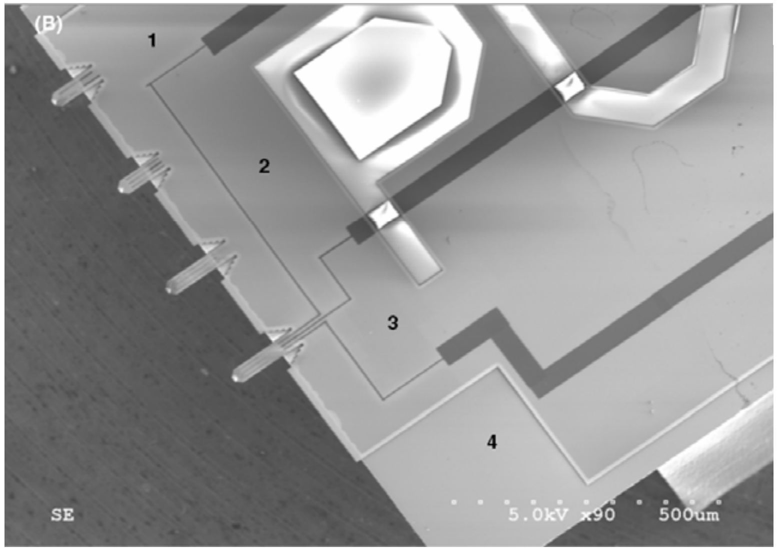
SEM images of the four-point AFM probe, (*A*) before and (*B*) after FIB fabrication(21)

Silicon nitride bio-AFM probe

Dimension: 100μm ×30μm ×0.18μm
Tip height: 7.0μm
Spring constant: 6pN/nm
(The probe is coated with 30nm gold film)

- The electrodes were introduced by fabricating three slits at the tip of the cantilever utilizing a focused ion beam system (FIB). The spacing of the two inner electrode pair (electrode 2, 3) is approximately 300nm and those of the outer pairs (electrodes 1, 2 & 3, 4) is approximately 1.0μm.

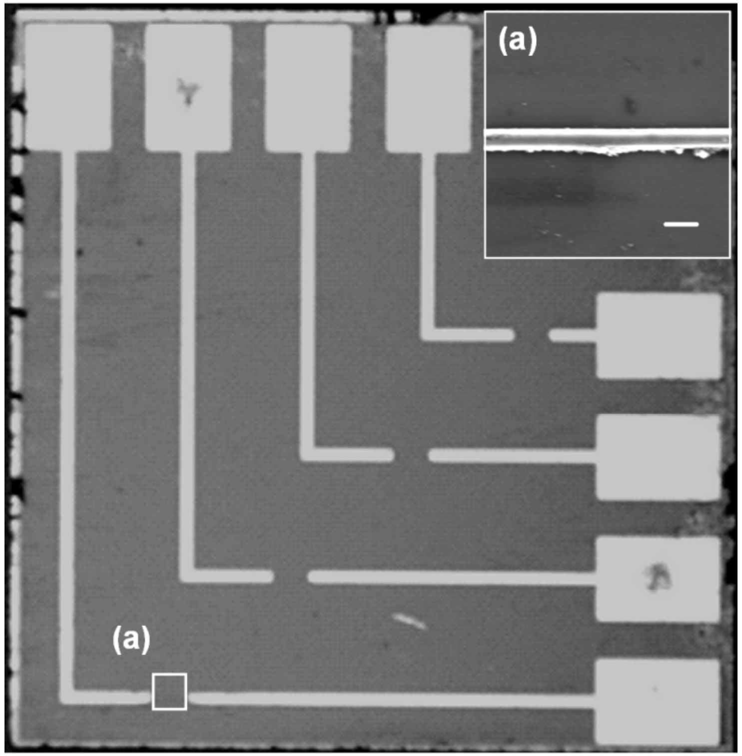
Fabrication of four-point AFM probe



The well-defined circuitry on the probe surface and substrate for the purpose of applied current and electrical potential drop measurements(21)

- The gold film was etched to form four disconnected conducting paths.
- The device allows simultaneous current transmission and detection of electrical potential drop.

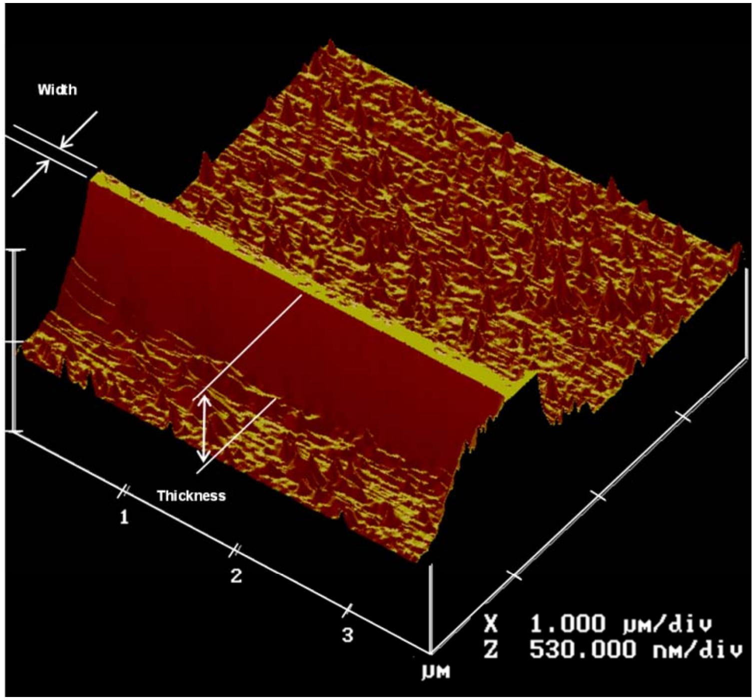
A nanowire sample and its AFM image



Optical image showing the 99.999% Al wire that was prepatterned by using sputtering and ion etching techniques. The inset is an SEM image of the wire that gives more details of its profile and dimensions (scale bar, 500 nm) (21)

- A 99.999% aluminum wire with a width of 400 nm and a thickness of 200 nm was patterned by a typical procedure of sputtering and ion etching.
- The wire was on a TiN (200 nm) /SiO_2 (200 nm) / Si (525 μm) substrate.

A nanowire sample and its AFM image



AFM topography images of the Al wire, which were obtained by the four-point AFM probe(21)

Surface topography obtained by the four-point AFM probe

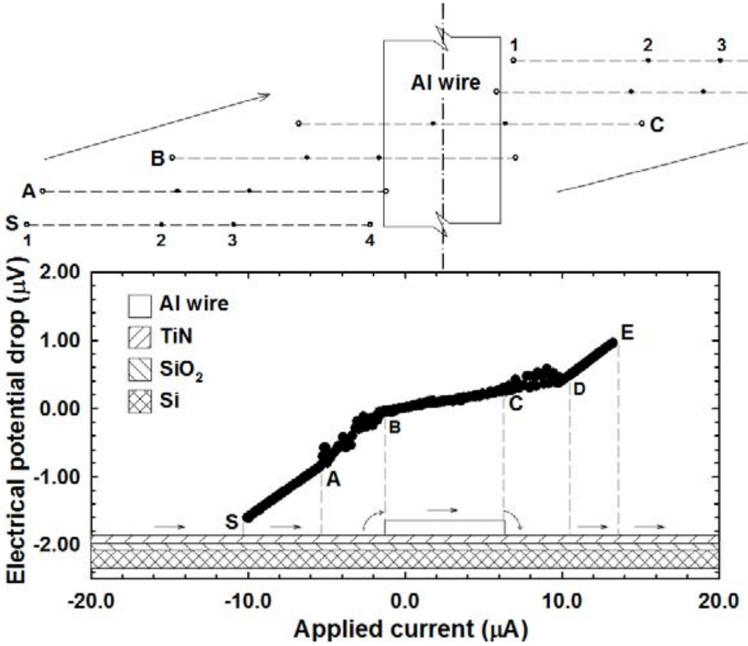
The scanning area: 4.0×4.0 µm

The scanning rate: 0.25 Hz

The measurements were reproducible, but a few fuzzy scratches were observed.

Splitting the tip of the probe into four electrodes may generate potential wobble induced by the force inhomogeneity.

Measuring the conductivity of nanowire



Typical current-voltage relationship of Al wire obtained by the four-point AFM probe technique(21)

During scanning, the two outer electrodes act as the current source and drain, while the inner ones measure the electrical potential drop using a digital voltmeter.

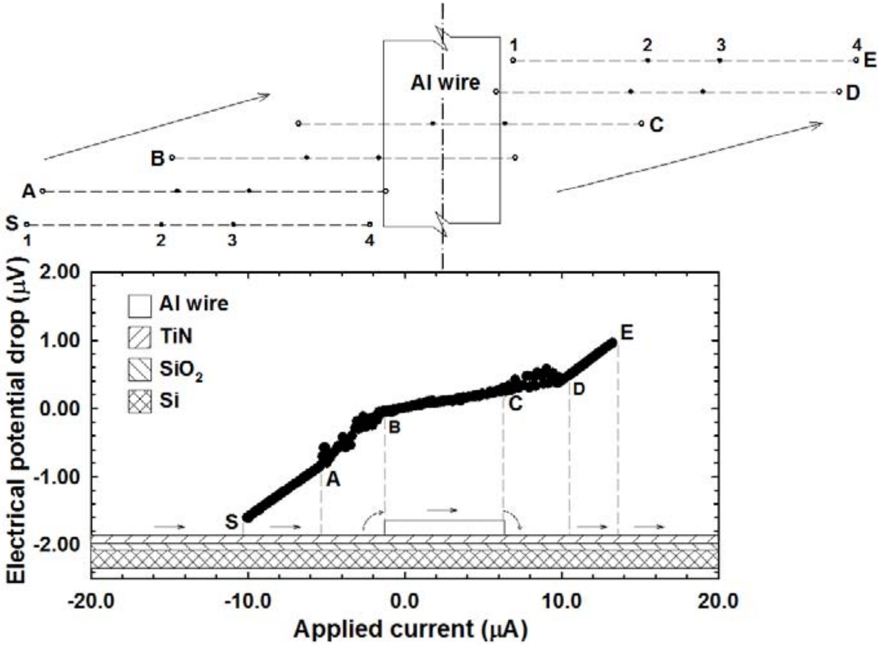
(i) S-A: Scan of the surface of TiN

- The slope of S-A is corresponding to the conductivity of TiN.

(ii) A-B: Moving of the electrodes across the edge of the nanowire

- The slope of A-B indicates the average of conductivities of TiN substrate and of the Al nanowire.

Measuring the conductivity of nanowire



Typical current-voltage relationship of Al wire obtained by the four-point AFM probe technique(21)

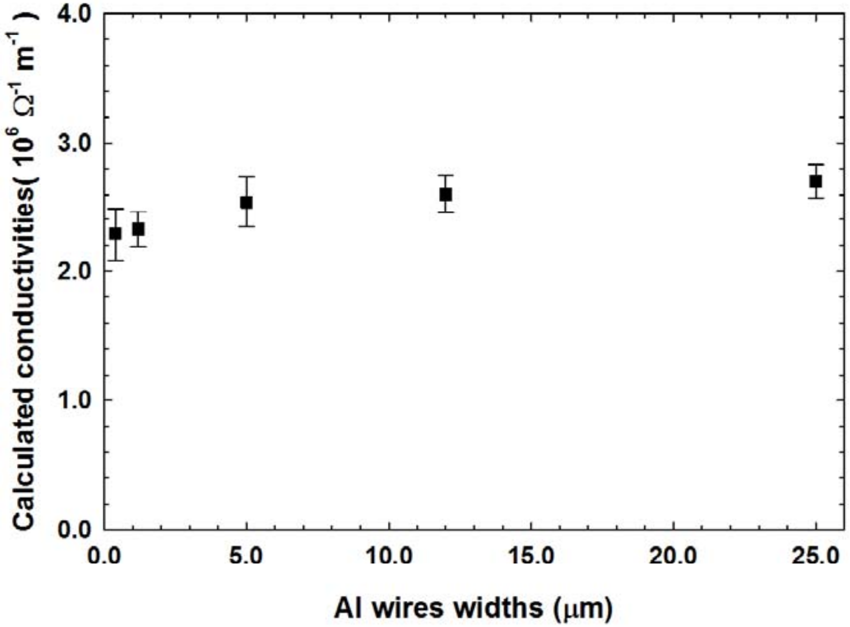
(iii) B-C: The two inner electrodes located on the Al nanowire and the two outer electrodes located on the surface of TiN

- The slope of B-C is corresponding to the conductivity of the Al nanowire.

(iv) C-D: The electrodes going down from the nanowire in sequence, a situation similar to that of case (ii).

(v) D-E: The electrodes scanning the TiN substrate again, similar to case (i).

Measuring the conductivity of nanowire



The calculated conductivities of the Al wires with the same thickness but different widths of 400 nm, 1.2 μm, 5.0 μm, 12.0 μm and 25.0 μm. The current-voltage measurement for each wire was carried out ten times, the error bars correspond to the ± mean SD(21)

- Since AFM image can provide simultaneously the dimensions of the wire at the nano-level, this ensures the precision of the conductivity calculation.
- The calculated conductivities are comparable with each other.

This work provides a basis for fast *in situ* characterization and fault-finding of submicron interconnects in nanocircuits and nanodevices.

1. The recent researches

2. Four-point probe method

3. Four-point AFM probe method

4. Microwave AFM method

Measurement of the topography and distribution of electrical properties of nanomaterials simultaneously

Microwave AFM Method

An evaluation apparatus which has the spatial resolution of nanometer scale

Scanning probe microscope (SPM)

- Scanning tunneling microscope (STM)
- Atomic force microscope (AFM)
- Near-field scanning optical microscope (NSOM)

The improved SPMs made it possible to measure not only the topography of materials but also the thickness of oxidized membrane, the profile of the two-dimensional dopant (22), the distribution of the electrical potential and the magnetic field on the material surface (23), the distribution of the hardness and stiffness on the material surface (24) and so on in nanometer order.

(22) Kopanski JJ et.al., (1996) J Vac Sci Technol B 14:242-247
(23) Martin Y et.al., (1988) Appl Phys Lett 52:1103-1105
(24) Petzold M et.al.,(1995) Thin Sol Films 264:153-158

Microwave AFM Method

Microwave microscope

The measurement of electrical properties and the detection of defects in the microscopic region

- Duewer et al. (25) succeeded in measuring resistivity of Cr, Zr and Mn by using the characteristic of microwaves that the resonant frequency changes depending on the capacitance between a probe tip and a material surface.
- Tabib-Azar and Akiwande (26) were successful in detecting and imaging depletion regions in solar cell p-n junctions in real time with the evanescent microwave probe.
- Ju et al. (27)were successful in the detection of delamination in integrated circuit packages by applying the properties of microwaves signals that change depending on the electrical properties of materials.

Necessity of keeping the standoff distance between a microwave probe and sample constant

(25) Duewer F et.al., (1999) Appl Phys Lett 74:2696-2698
(26) Tabib-Azar M, Akiwande D, (2000) Rev Sci Instrum 71:1460-1465
(27) Ju Y, et.al., (2001) IEEE Trans Instrum Meas 50:1019-1023

Microwave AFM Method

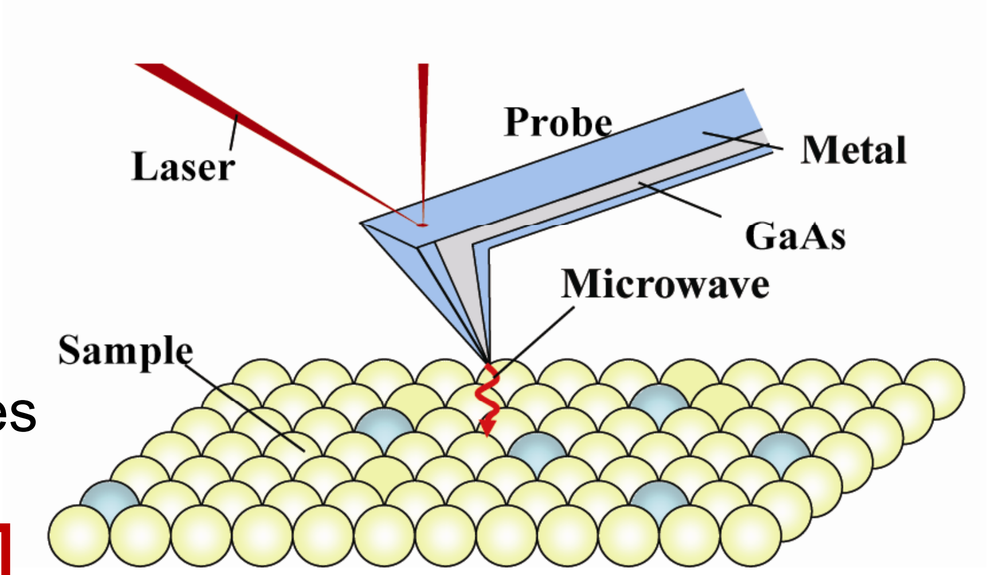
New SPM system for measurement of electrical properties, conductivity, permittivity and permeability, in local area

Atomic Force Microscope

- High spatial resolution
- Standoff distance control in high precision

Microwave technique

- Evaluation of electrical properties

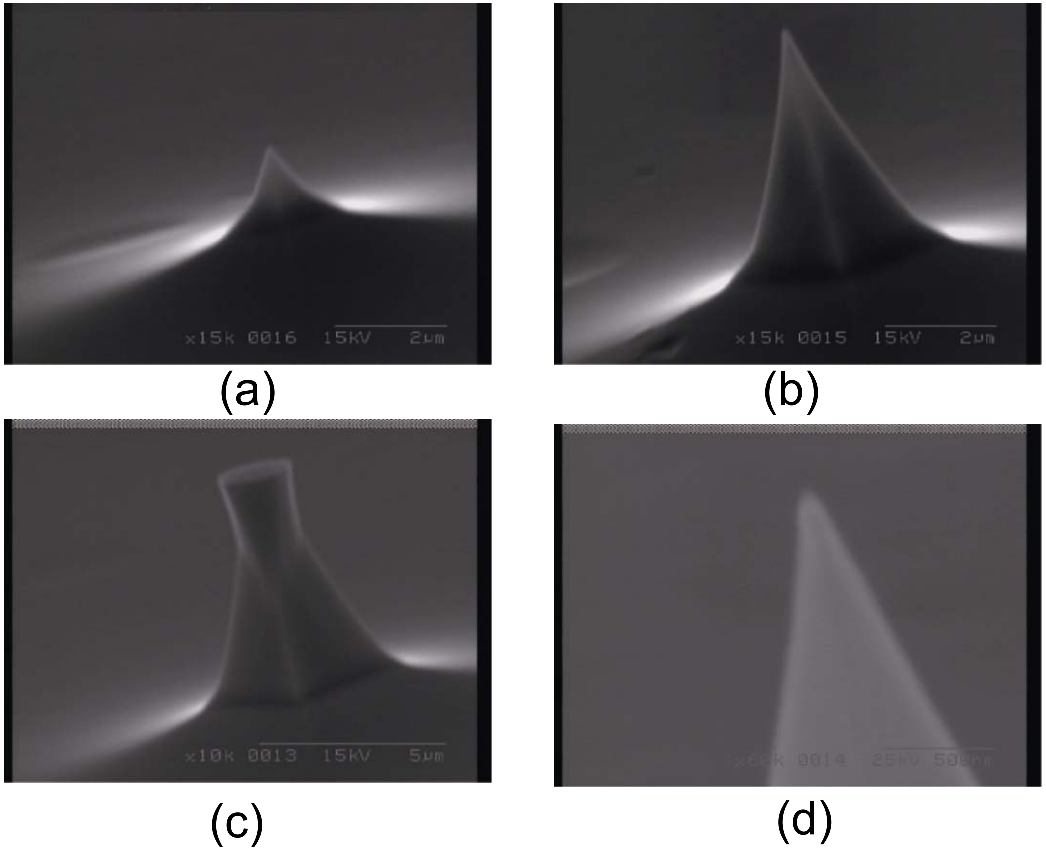


Schematic diagram of the M-AFM probe used for measuring the electrical properties of materials

Microwave Atomic Force Microscope (M-AFM)(28)-(31)

(28) Ju Y et.al., (2005) Proc interPACK 2005 (CD-ROM):73140
(29) Ju Y et.al., (2007) Proc interPACK 2007 (CD-ROM):33613
(30) Ju Y et.al., (2008) Microsyst Technol 14:1021-1025
(31) Ju Y et.al., (2009) Microsyst Technol 15:1195-1199

Fabricating the Tip of M-AFM Probe



SEM photograph of the tips fabricated by etching masks with different dimensions: (a) by 13 μm etching mask; (b) by 14 μm etching mask; (c) by 15 μm etching mask; (d) enlarged part of the tip fabricated from 14 μm etching mask(28)

M-AFM probe of made of GaAs substrate

- The attenuation of microwave
- A side-etching property by wet etching
- A sphalerite structure

One side of the square mask being 45° to the <011> direction can form a tip with a higher aspect ratio comparing with the case of one side of the resist pattern being parallel to <011> direction.

Fabrication of M-AFM Probe

Substrate

- plane direction (1 0 0)
- thickness 350 μm
- undoped (semi-insulating)

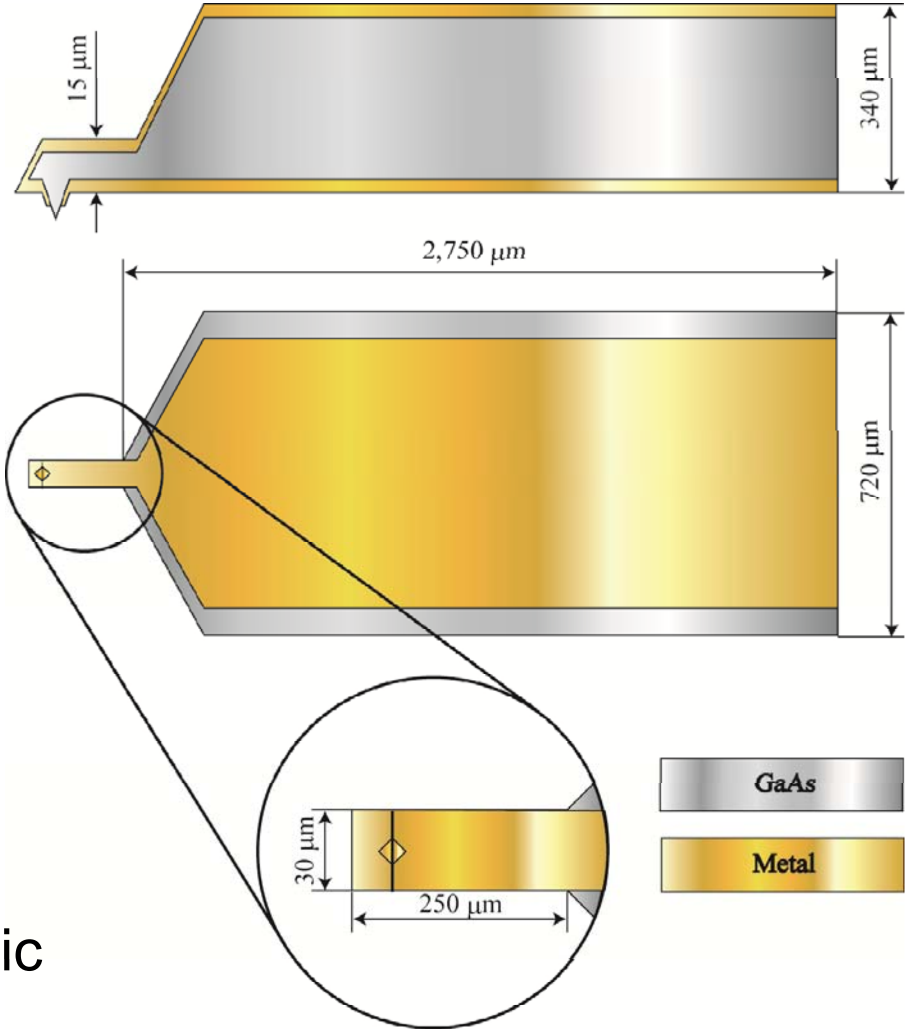
Dimensions

Cantilever

250 × 30 × 15 μm

Holder

2,750 × 720 × 340 μm



The waveguide having a characteristic impedance of 50Ω

Fabrication of M-AFM Probe

a. Patterning of the etching mask for the tip fabrication

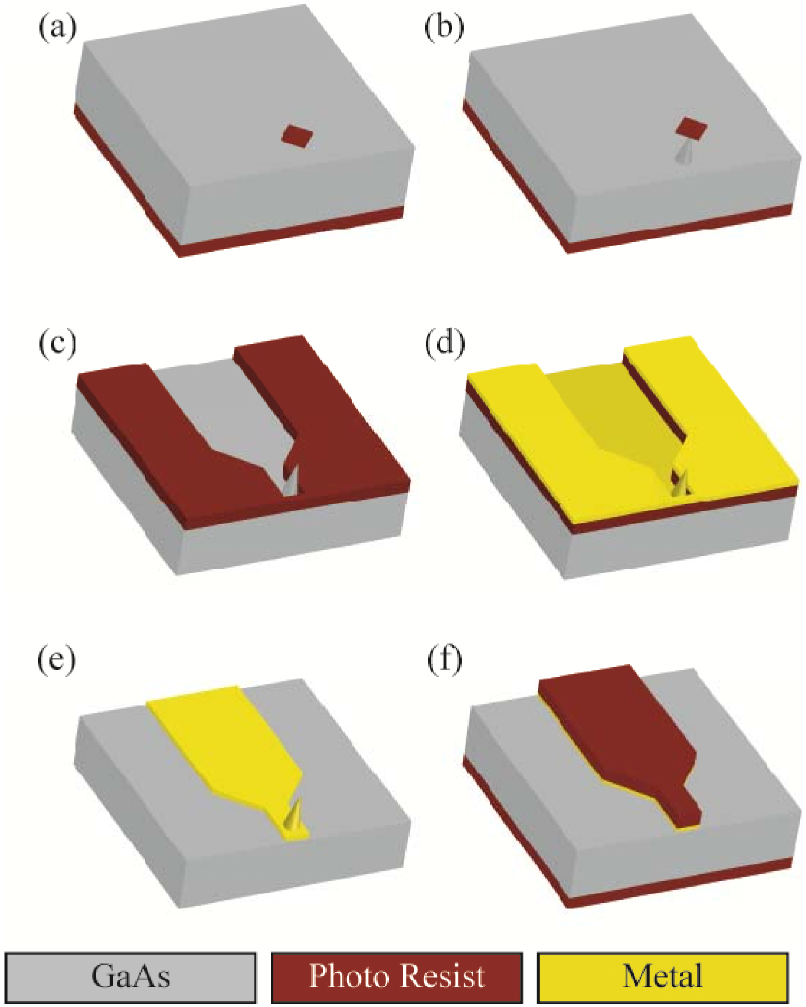
b. Forming the tip of the probe by wet etching

c. Patterning of the stencil mask for the waveguide on the top surface

d. Coating the metal film on the top surface

e. Forming the waveguide by lift-off process

f. Patterning of the etching mask for the cantilever fabrication



Fabrication of M-AFM Probe

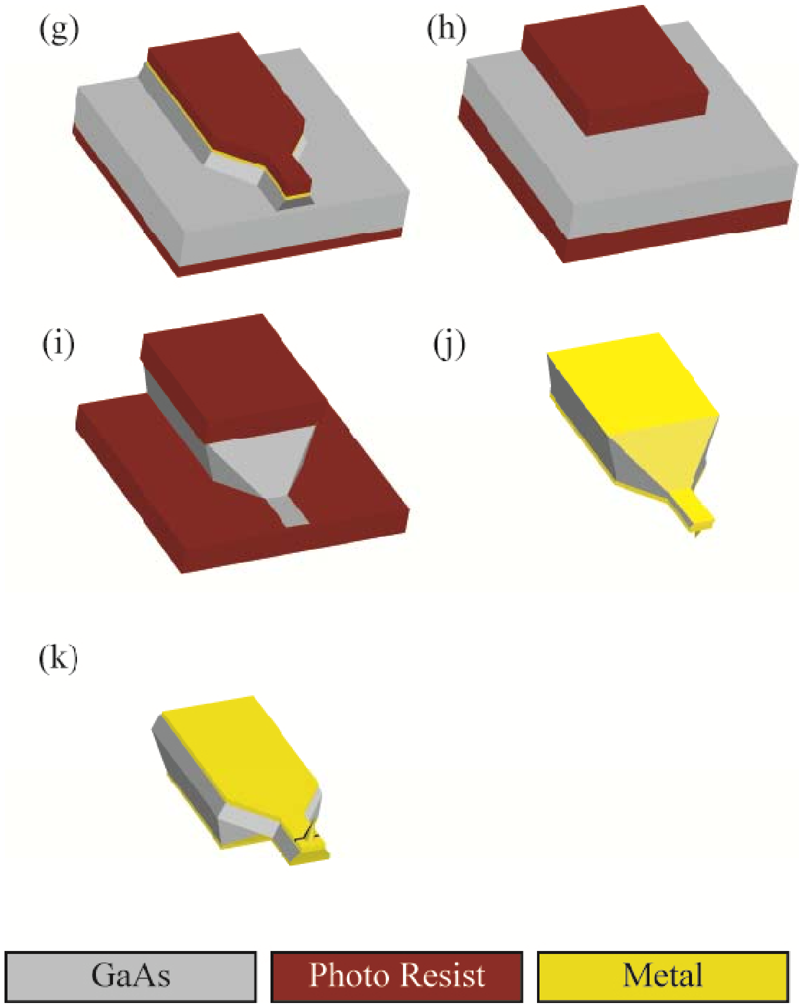
g. Forming the cantilever of the probe by wet etching

h. Patterning of the etching mask on back side for the holder fabrication

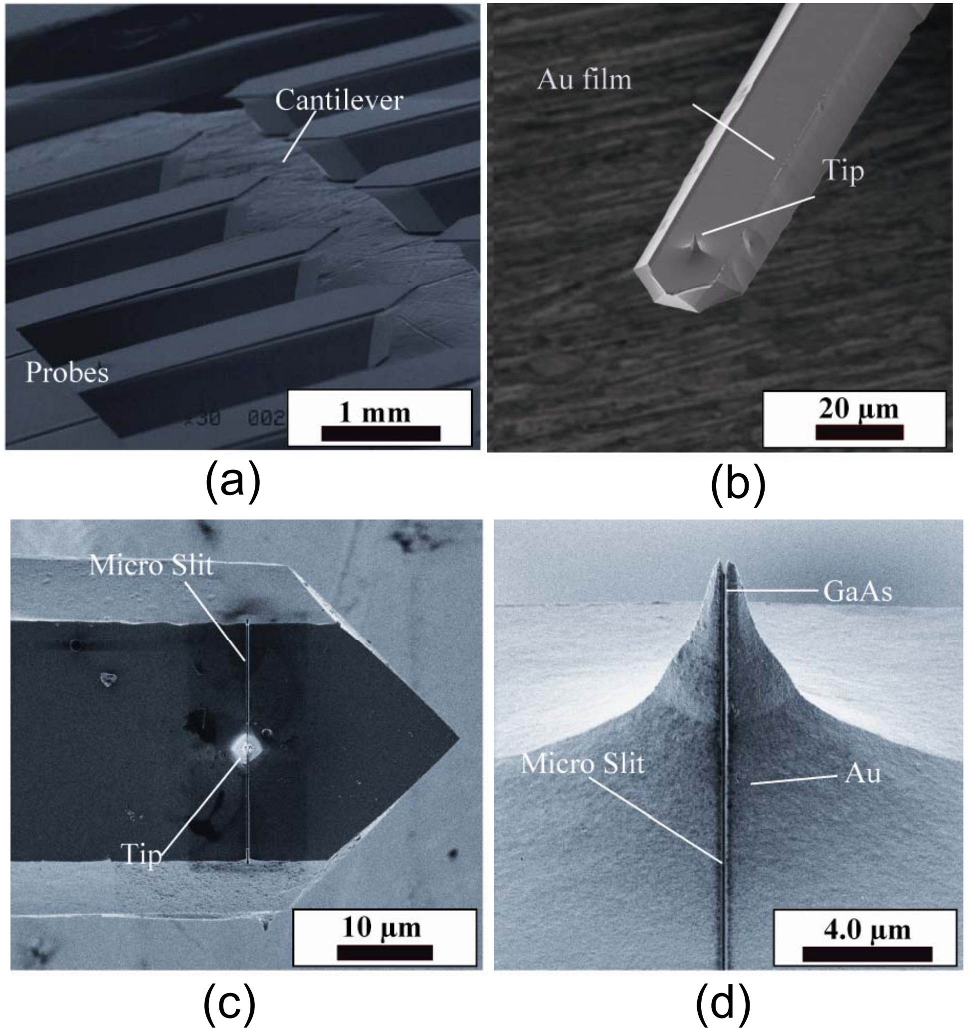
i. Forming the holder of the probe by wet etching

j. Coating metal film on the bottom surface to form the waveguide

k. Forming the open structure at the tip of the probe by FIB fabrication



Fabrication of M-AFM Probe



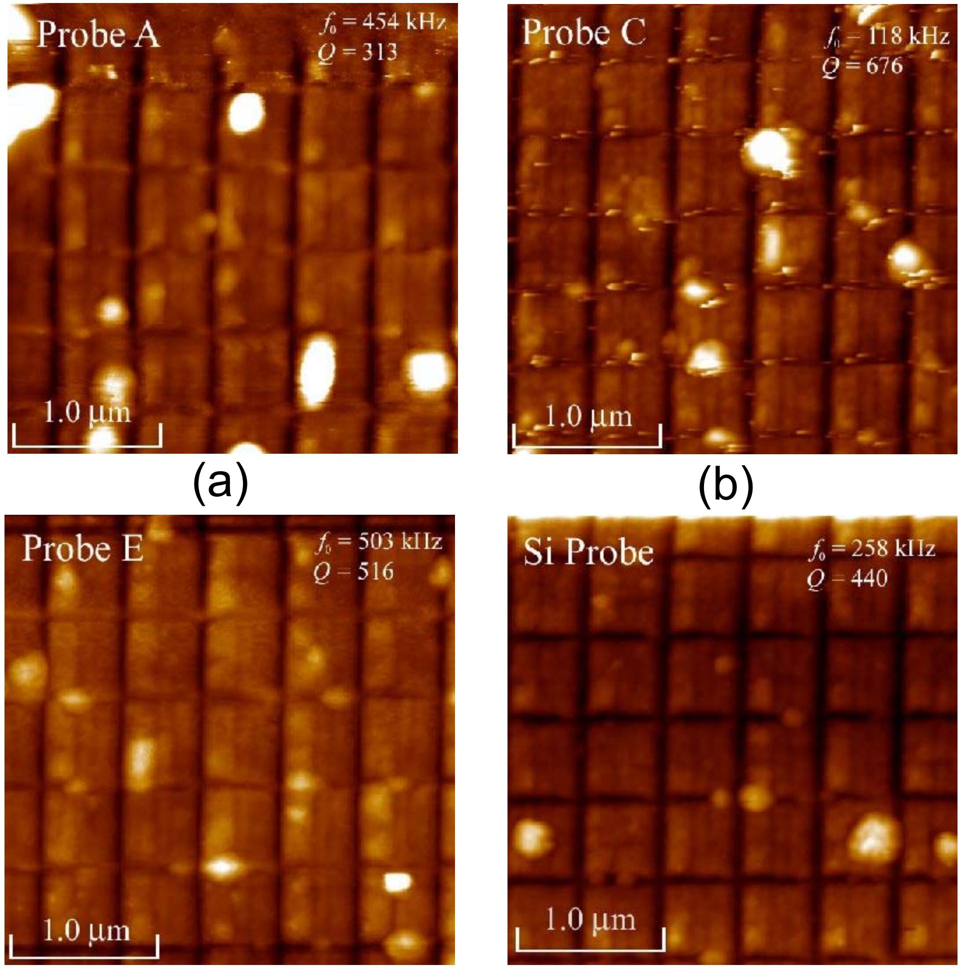
(a) (b) (c) (d)

SEM photograph of the fabricated M-AFM probes

(a) The M-AFM probes on a quarter of GaAs wafer
(b) A cantilever of the M-AFM probe
(c) A micro slit introduced across the cantilever through the center of the tip with the width no more than 100 nm
(d) High-magnification image of the tip

The tip height:
8 µm
Dimensions of the cantilevers:
254×31.6×11.1 µm
Dimensions of the bodies of the probes:
2743×721×338 µm
The value of the characteristic impedance:
35.7 Ω

Measuring Topography by M-AFM Probe



(a) (b)

(c) (d)

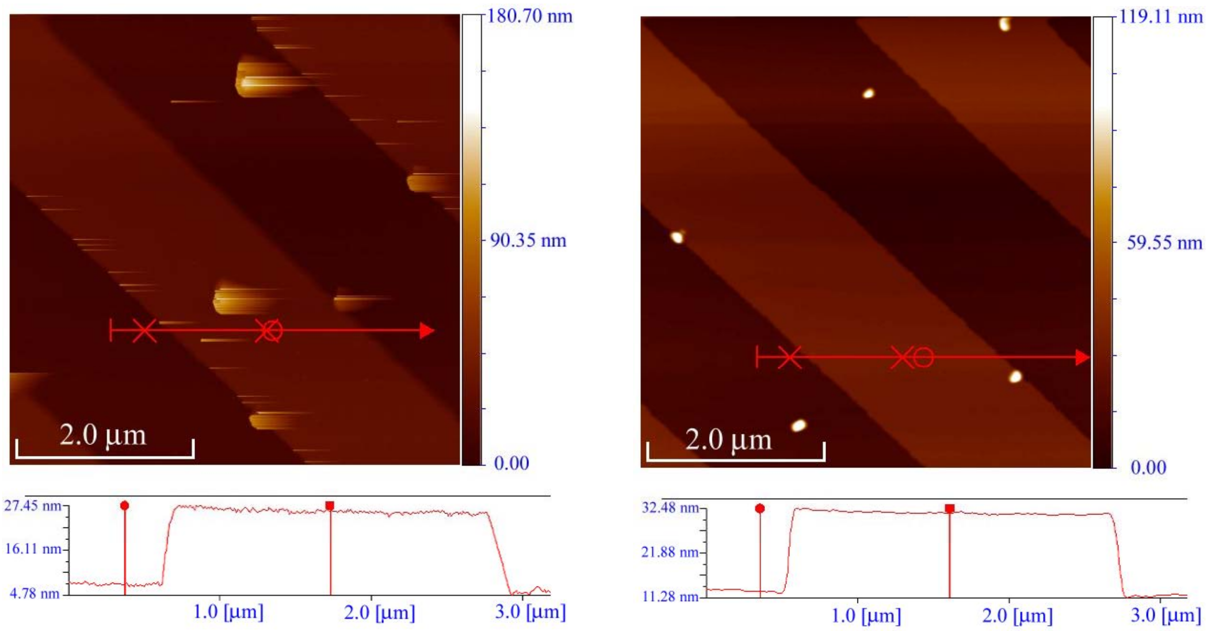
Surface topography of the grating sample measured by different probes(30)

The AFM topography of grating sample having 2000 line/mm
Scan area: 3 × 3 μm^2

(a) M-AFM probe A
(b) M-AFM probe C
(c) M-AFM probe E
(d) Commercial Si probe

- ➢ The commercial Si probe still can obtain higher resolution topography due to the higher aspect ratio of the tip.
- ➢ M-AFM probe has a similar capability for sensing surface topography of materials as that of commercial AFM probes.

Measuring Topography by M-AFM Probe



(a) (b)

Surface topography and scanning profile of the grating sample measured by different probes: (a) M-AFM probe C; (b) commercial Si probe(30)

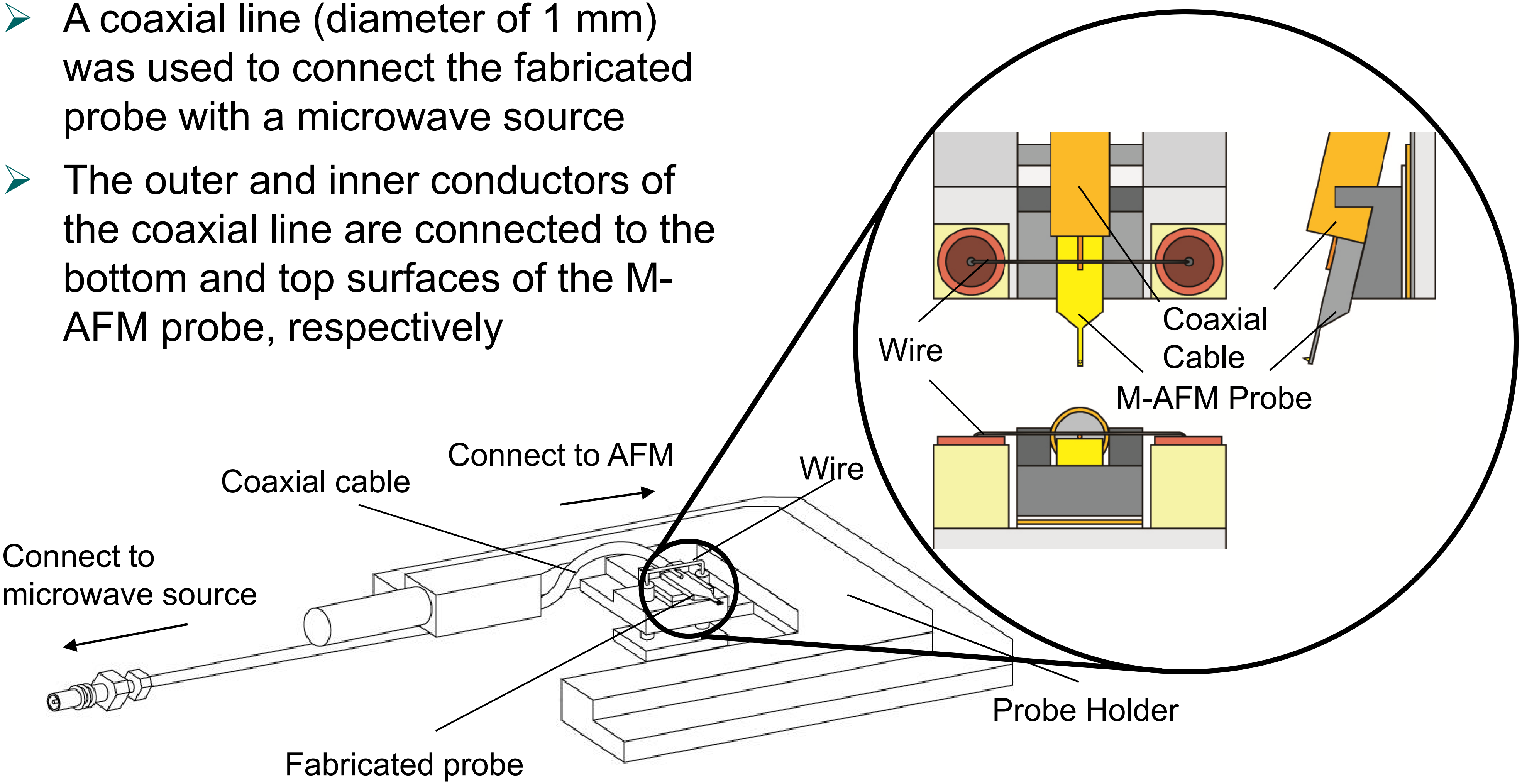
The AFM topography of grating sample having 17.9 nm step height

(a) The step height of M-AFM probe:
18.60 nm

(b) The step height of the commercial Si probe:
18.62 nm

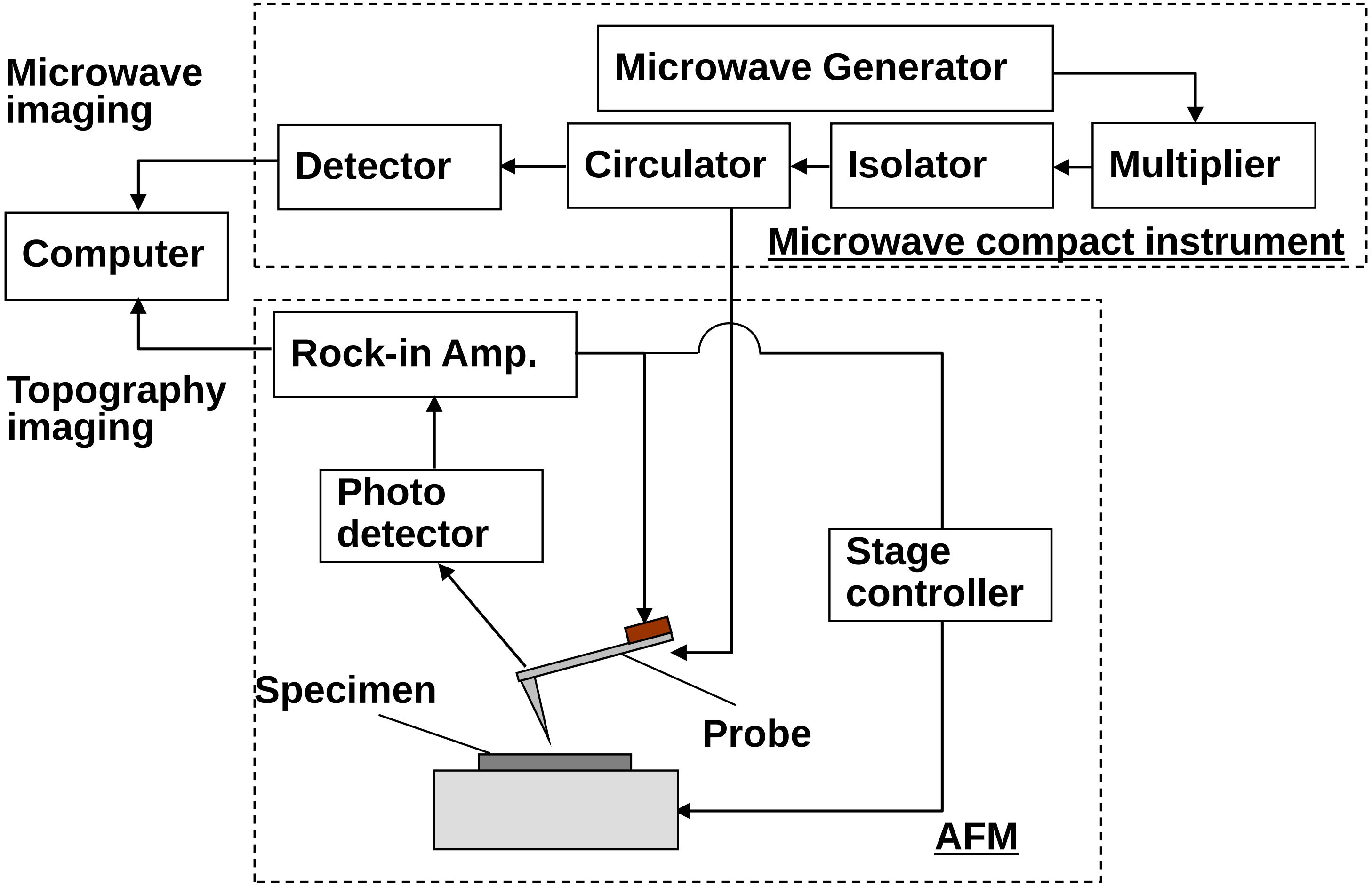
Connection of the fabricated probe and a microwave source

- A coaxial line (diameter of 1 mm) was used to connect the fabricated probe with a microwave source
- The outer and inner conductors of the coaxial line are connected to the bottom and top surfaces of the M-AFM probe, respectively



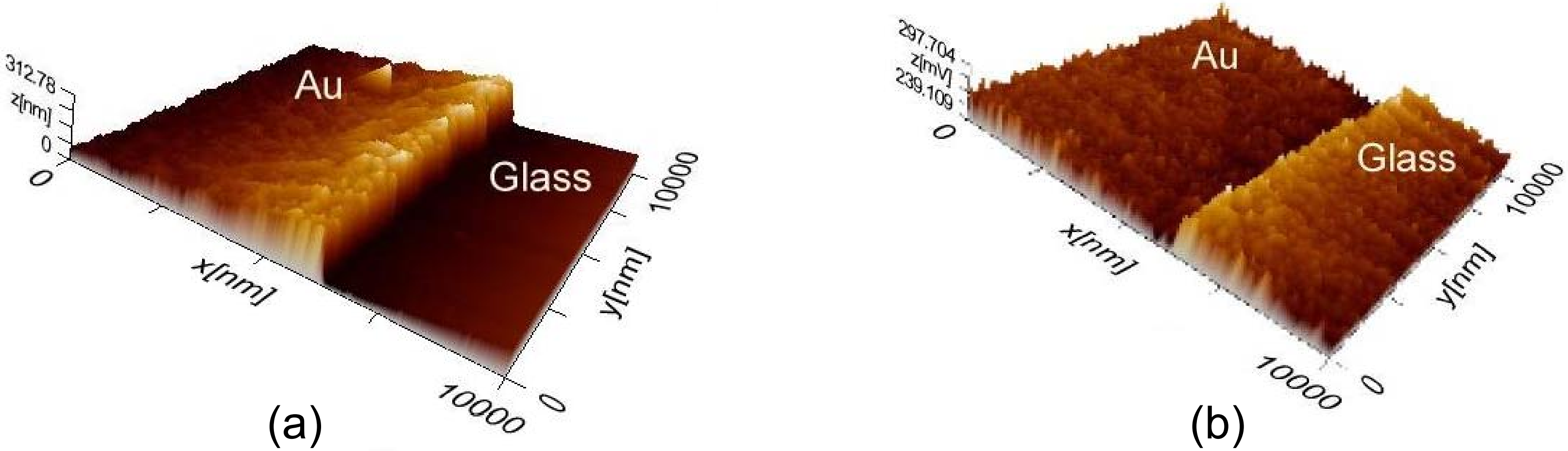
Measurement Using M-AFM

- The connection of the AFM with the microwave instrument



The schematic diagram of the M-AFM system

Microwave Image Obtained by M-AFM



(a) (b)

M-AFM images: (a) AFM topography image of the sample (Au film coating on glass wafer substrate) obtained by the M-AFM probe, (b) microwave image by converting the measured microwave signals into the voltage without calibration(32)

- M-AFM working mode: noncontact
- Scanning speed: 5μm/sec
- Scanning area: 10μm × 10μm (the step area between the Au film and glass wafer substrate)

(a) Average Au film thickness: 207 nm

(b) Measured outputting voltage

Au: 265 mV, Glass: 285 mV

(32) Zhang L et.al.,(2010) Rev Sci Instrum 81:123708(1-4)

Measurement of Electrical Properties by M-AFM

Since the reflection from bottom surface can be neglected, the measured reflection coefficient of the microwave signal can be expressed by considering the reflection only from the top surface as(33)

$$\Gamma = \frac{\eta - \eta_0}{\eta + \eta_0} \qquad \left(\eta = \sqrt{\frac{\mu}{\varepsilon - j\dfrac{\sigma}{\omega}}} \qquad \eta_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \right)$$

Γ represents the reflection coefficient, and η, σ, μ, and ε are intrinsic impedance, conductivity, permeability, and permittivity of materials, respectively, and η_0, σ_0, μ_0, and ε_0 are those of free space. Symbol denotes the angular frequency, and $j = \sqrt{-1}$.

(33) Pozar DM (1998) Microwave Engineering, Second Edition. John Wiley & Sons, N.Y.

Measurement of Electrical Properties by M-AFM

For non magnetic materials, considering $\mu=\mu_0$, and using the above equations, the reflection coefficient, Γ, can finally be written as(34)

$$\Gamma = X + jY = \frac{1-\sqrt{\dfrac{\varepsilon}{\varepsilon_0} - j\dfrac{\sigma}{\omega\varepsilon_0}}}{1+\sqrt{\dfrac{\varepsilon}{\varepsilon_0} - j\dfrac{\sigma}{\omega\varepsilon_0}}}$$

X : the real part of the reflection coefficient.
Y : the image part of the reflection coefficient.

By solving the simultaneous equations of the real and imaginary parts of the equation and eliminating *e*, the conductivity of materials can be expressed as

$$\sigma = \frac{4\omega\varepsilon_0 Y(1-X^2-Y^2)}{[(1+X)^2+Y^2]^2}$$

(34) Ju Y et.al., (2002) Appl Phys Lett 81:3585-3587

Measurement of Electrical Properties by M-AFM

On the other hand, the amplitude, $|\Gamma_m|$, and the phase, θ_m, of the measured reflection coefficient, Γ_m, can obtained by microwave measurement using following equation

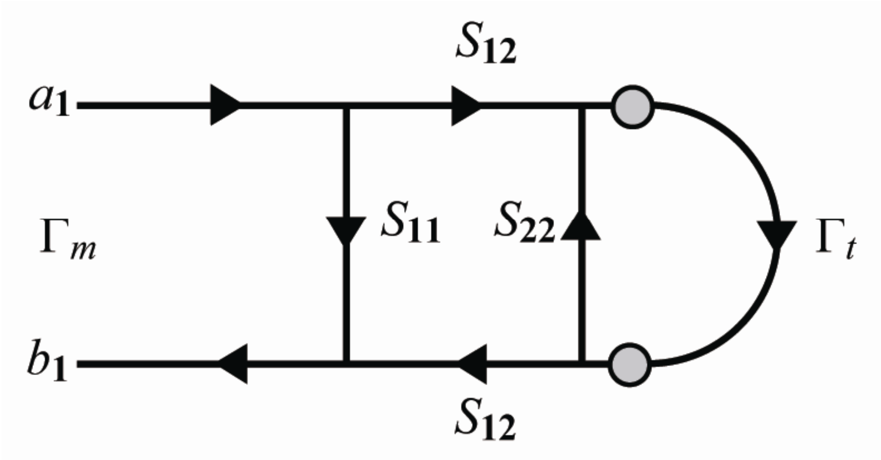
$$\Gamma_m = |\Gamma_m| e^{j\theta_m}$$

Here, Γ_m is influenced by not only the electrical conductivity of metals but also the standoff distance, reflection generated at the aperture part of the probe, the connection parts between the probe and coaxial line, and so on. Therefore, to examine a correct value of σ, we must find the theoretical reflection coefficient Γ_t by calibrating the measured Γ_m.

Measurement of Electrical Properties by M-AFM

By using, S_{11}, S_{12}, S_{22}, and Γ_t, Γ_m can expressed as(33)

$$\Gamma_m = \frac{b_1}{a_1} = S_{11} + \frac{S_{12}^2 \Gamma_t}{1 - S_{22}^2 \Gamma_t}$$



Signal flow graph for the reflection measurement

where $a_1$and $b_1$are input and output of microwave signal, S_{11}, S_{12} and S_{22} are errors of the measurement system including losses and phase delays caused by the effects of the connectors, cables and the M-AFM probe.

Measurement of Electrical Properties by M-AFM

By solving the equation of previous page, the theoretical reflection coefficient can expressed as

$$\Gamma_t = \frac{\Gamma_m - S_{11}}{S_{12}^2 + S_{22}(\Gamma_m - S_{11})}$$

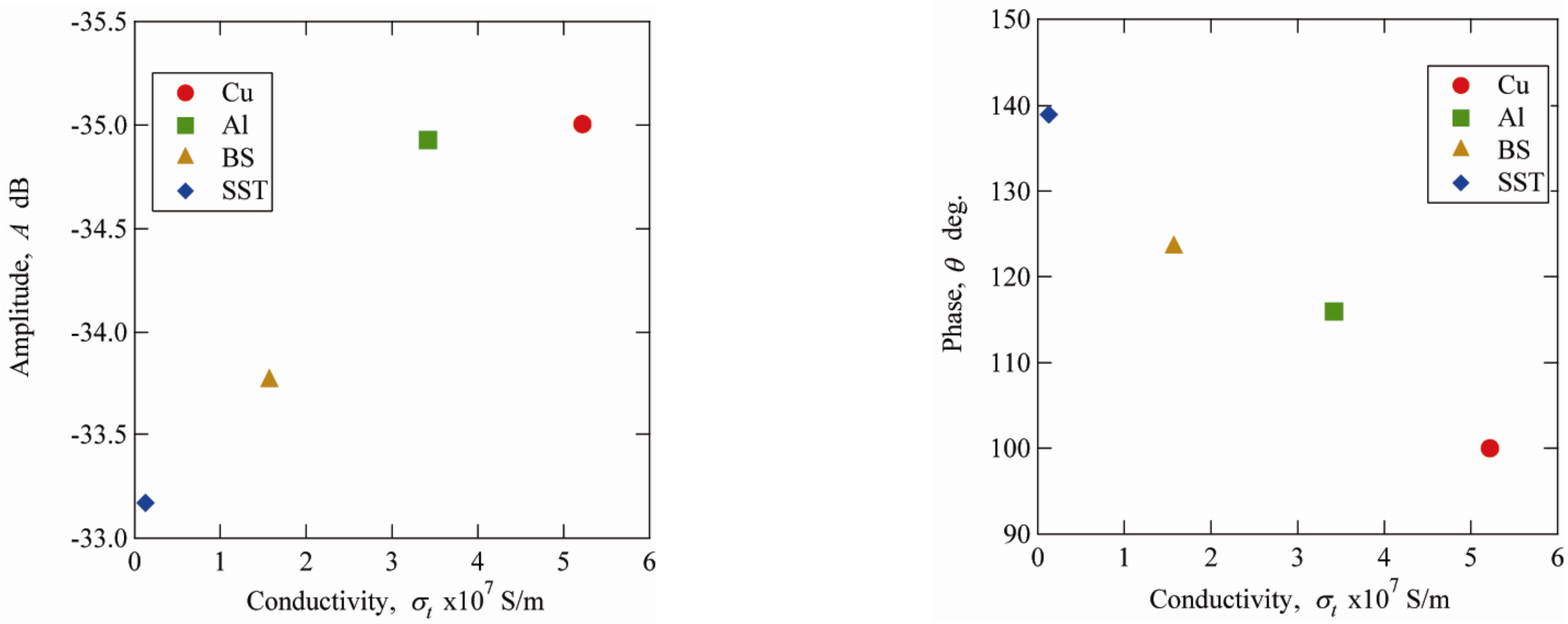
$$S_{22} = \frac{(\Gamma_{t1} - \Gamma_{t2})(\Gamma_{m2} - \Gamma_{m3}) - (\Gamma_{t2} - \Gamma_{t3})(\Gamma_{m1} - \Gamma_{m2})}{\Gamma_{t3}(\Gamma_{t1} - \Gamma_{t2})(\Gamma_{m2} - \Gamma_{m3}) - \Gamma_{t1}(\Gamma_{t2} - \Gamma_{t3})(\Gamma_{m1} - \Gamma_{m2})}$$

$$S_{12}^2 = \frac{(\Gamma_{m1} - \Gamma_{m2})(1 - S_{22}\Gamma_{t1})(1 - S_{22}\Gamma_{t2})}{\Gamma_{t1} - \Gamma_{t2}}$$

$$S_{11} = \Gamma_{m1} - \frac{S_{12}^2\Gamma_{t1})}{1 - S_{22}\Gamma_{t1}}$$

Measurement of Electrical Properties by M-AFM

The measured amplitude and phase of the reflection coefficient verses the electrical conductivity, for a sample with cupper (Cu), aluminum (Al), brass (BS) and stainless steel (SST) surfaces, by a M-AFM probe(35)

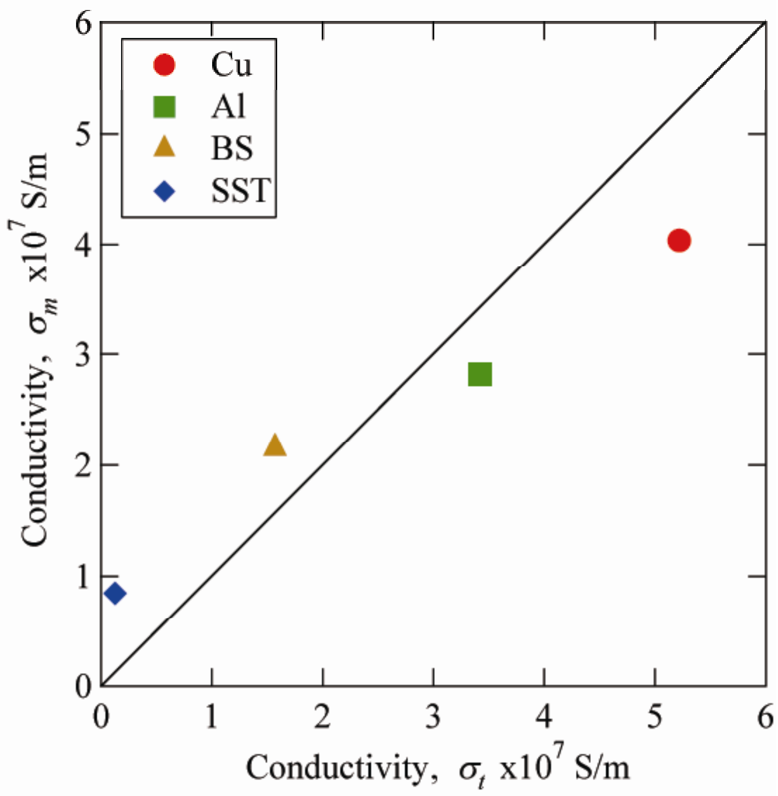


(a) (b)

Results of microwave measurement: (a) the relationship between the amplitude of reflection coefficient and the electrical conductivity; (b) the relationship between the phase of reflection coefficient and the electrical conductivity

(35) Fujimoto A et.al., (2011) Microsyst Technol 17:(in press)

Measurement of Electrical Properties by M-AFM



The relationship between the conductivity, σ_m, obtained by the microwave measurement and the conductivity, σ_t, measured by a high-frequency conductometry(35)

- Each σ_m was obtained by carrying out the calibration as described above using the other three ones as the references.

These results indicate that the microwave measurement can discriminate the conductivity of the metallic micro and nano materials quantitatively.