CHAPTER THREE: MEASUREMENT TECHNIQUES AND EXPERIMENTAL DETAILS

In section 3.1, the working principles of main instruments used in this project are discussed. This is followed by the explanation of experimental setup in section 3.2.

3.1 Working principle of main instruments used in the project

3.1.1 Atomic Force Microscope (AFM) [47-48]

AFM is capable of measuring tiny forces that exist by virtue of van der Waals, resonant change, electrostatic and magnetic interactions between atoms of the tip and sample. Although extremely small, these forces are large enough to push the tip away, provided it is on a flexible, highly compliant cantilever.

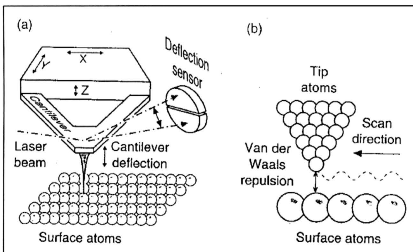

Figure 3.1: Working principles of the AFM, showing (a) the laser reflection technique for measuring cantilever deflection, and (b) a cluster of atoms on the tip sensing van der Waals forces near the surface [47].

Figure 3.1 shows the typical configuration of an AFM. The tip is fastened to a flexible cantilever, which in turn is mounted to piezoelectric drivers for X, Y and Z movements. Often, the tip and cantilever are fabricated concurrently from the same material, which typically is SiO_2 or Si_3N_4. At a given point over the sample, atomic level interactions may repel or attract atoms cluster of the tip and push it away, or pull it towards the surface. The cantilever bends more over elevated points on the sample, and less over depressions. In this way, it is possible to map out roughness point by point across the surface without ever making direct contact. In practice, the tip and cantilever are usually raised and lowered to maintain a constant gap, or cantilever deflection. The vertical motion is sensed by observing the deflection of a narrow laser beam that is reflected from the back of the cantilever.

AFM can be operated in non-contact mode, contact mode or tapping mode, as illustrated in Fig. 3.2 (a), (b) and (c).

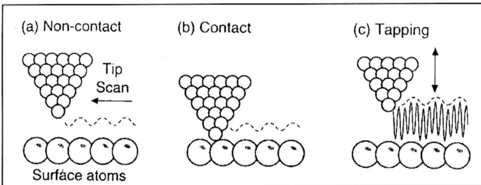

Figure 3.2: AFM can be operated in either non-contact or contact modes, but tapping mode is more universally practiced [47].

The tip uses in contact mode is generally more robust because the forces involved are larger, although it is more prone to inflict damage to the sample. However, it is found that using tapping mode, as illustrated in Fig. 3.2 (c) can minimize surface

damage during measurement. Here, the tip is driven into the vertical oscillation at the resonant frequency of the cantilever. It touches the surface only briefly at the extreme of each down cycle. Therefore, the physical contact with the sample is kept to a minimum. In the tapping mode, the force at the tip is not measured directly as before, but is inferred from the way it changes the amplitude or resonant frequency of the cantilever. Normally, the cantilevers have resonant frequency between 10 – 120 kHz.

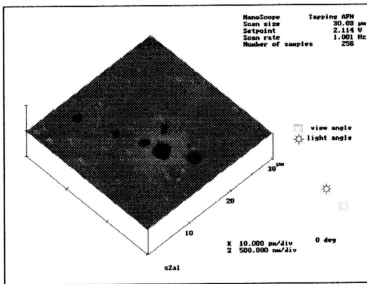

Figure 3.3: Etch pits are observed on silicon wafer surface after Secco etching (potassium:HFW:HF =132.2 gm: 3 L: 6 L, 30 minutes). The image is captured using AFM in tapping mode. The scanning size of the image is 30 x 30 μm^2 and scan rate is 1.0Hz.

The main applications of AFM in S.E.H. (M) Sdn. Bhd. are to measure surface micro roughness, micro scratches, size of particles and D-defects. Moreover, it is used to distinguish between small particles and voids with size around 0.1 – 3.0 µm. By using an in-house developed Defect Detection System (DDS) [49], one is able to register the coordinates of a surface defect as small as >

0.10 μm. Then, one can go back to the location repeatability with offset within ±10μm using AFM.

3.1.2 Time Of Flight – Secondary Ion Mass Spectroscopy (TOF-SIMS)

TOF-SIMS has high sensitivity (in ppb range) to most elements in the periodic table. It offers a unique combination of small analytical spot and high sensitivity for detecting thin film organic and metallic materials on the surface. It employs a primary-ion fluence of $< 10^{14}$ cm^{-2} that leaves the sample surface relatively undisturbed. The rate of removal of material from the sample is so low under such conditions that only a fraction of a single surface monolayer is removed in an hour. Hence, TOF-SIMS is effectively non-destructive and suited for applications to thin films of surface contamination.

In this technique, there are two types of ions, namely primary ions and secondary ions. Primary ions are used to sputter away atoms\ions from a sample surface. Liquid Ga^{+} ion gun of the type illustrated in Fig. 3.4 is regulary used for TOF-SIMS. This is because it is possible to form sharp nanosecond bursts of ions by pulsing the extraction field [47,50].

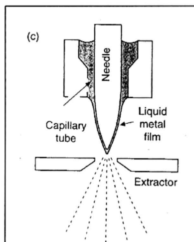

Figure 3.4: Sources of ions used in TOF-SIMS instrumentation. Ions are produced from liquid Ga in the liquid metal gun [47].

The ions that have been sputtered from a sample surface by bombarding with primary ions are known as secondary ions. These secondary ions are individually detected and tabulated as a function of their mass-to-charge ratio. This information is used to determine the composition of the surface.

As mentioned in above paragraph, TOF-SIMS distinguishes between ions of different mass (m) by measuring the time that they taken to travel the length of a fixed path, as illustrated in Fig. 3.5.

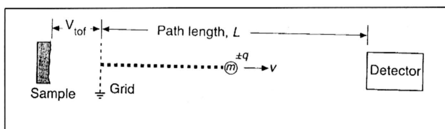

Figure 3.5: Basic principle of Time-of-flight mass spectrometer [47].

Fragments of charge q are extracted from the sample and accelerated through a field V_{tof} in advance of the path, so that they attain a velocity of v given by

$$\tfrac{1}{2} mv^2 = q\, V_{tof} \tag{12}$$

The flight time τ is then given by the path length L, divided by v, which from Eq. (12) and becomes

$$\tau = L\left(\frac{m}{2qV_{tof}}\right)^{1/2} \tag{13}$$

It is a strength and at the same time a weakness of TOF-SIMS that hundreds of peaks populate almost all of the organic spectra acquired from semiconductor samples. For example, the technique was applied as a simple photoresist cleanup monitor. The huge number of peaks found in the general spectrum (Fig. 3.6) presents the analyst with a serious problem of how to determine which segment of the spectrum, if any, is relevant to the cleanup issue at hand. Often, it takes a good organic chemist with experience in molecular fragmentation patterns to sort out the problem.

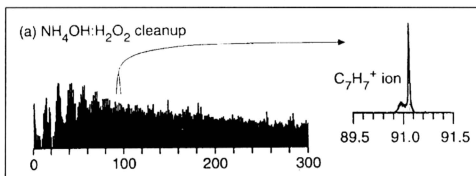

Figure 3.6: TOF-SIMS spectra showing the relative result of two photoresist cleanups on residual organics at the surface of a Si wafer. SC-15 (NH_4OH: H_2O_2: H_2O) is used in (a), with the same followed by HF in (b). Intensity of the $C_7H_7^+$ ion correlates with effectiveness of the cleanup [47].

The other weakness of TOF-SIMS is mass interference. Mass interference occurs when fragments from the sample combine with other atoms or molecules before entering the mass spectrometer. The problem is particularly troublesome when light elements like H, C, O and N from the vacuum system are available at the surface during sputter etching. For instance, a simple depth profile of P in Si is not as simple as straightforward as it seems. This is because the single isotope which is available, $^{31}P^+$, bears the same *m/q* ratio as the $^{30}Si^1H^+$ or $^{29}Si^1H_2$ molecules.

3.2 Experimental setup

3.2.1 General procedures of copper decoration process

Basically, there are 4 main steps in copper decoration process, i.e. (i) sample preparation, (ii) equipment preparation, (iii) copper decoration and (iv) counting defect density of copper decorated wafer.

(i) To prepare copper decoration samples, wafers are sent for thermal oxidation at selected temperature in order to grow a desired oxide thickness. Then, the oxide layer on the chemical treated surface is stripped off by using HF as shown in Fig. 3.7 (a). This is to obtain good electrical conductivity on this surface when the wafer is placed on top of the gold-coated cathode.

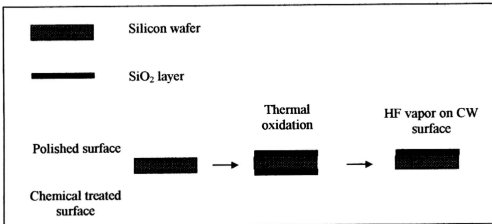

Figure 3.7 (a): Sample preparation in copper decoration technique.

(ii) Copper decoration unit needs to be cleaned prior copper decoration process. This is because copper oxide will grows on the surface of anode and cathode when they are exposed to atmosphere. Moreover, there will have some residual of metallic elements (especially copper) in the unit from previous copper decoration process. All of these might affect the repeatability and reproducibility of copper decoration results. Hence, the cleaning can be done by dipping the teflon beaker, glass plate, anode and cathode in diluted nitric acid ($\approx$ 1% vol.) for 1 minute. Then, these parts are rinsed with water to wash away the entire dirt and nitric acid. This is followed by pouring one liter of fresh electronic grade of methanol into the teflon beaker.

Next, one needs to introduce a certain amount of copper ions into the fresh methanol. This is to ensure the copper dots formed on the wafer surface at the later stage is sufficient large to be observed under low magnification of optical microscope (50X). To build up copper concentration in methanol, one piece of oxidized dummy wafer is loaded into the beaker. Then, a DC voltage of 15V is applied to copper decoration equipment. Since there is a current flows in the circuit, electrolysis process occurs. Copper ions are dissolved into the methanol. Normally, copper concentration in the methanol is sufficient after thirty minutes of seasoning stage. Then, the dummy wafer is removed from the equipment. At this stage, the copper decoration unit is ready for copper decoration.

(iii) To carry out copper decoration, sample is loaded into the equipment. Then, oxide layer of sample is stressed by a selected electric field for a certain period.

copper ions in the methanol is driven by the electric field and deposited on oxide surface. Consequently, copper dots are formed on the oxide surface.

(iv) The number of copper dots formed per cm^2, also knows as defect density, and is counted by using an optical microscope under low magnification (50X). The counting area is illustrated in Fig. 3.7 (b), lying across the diameter of wafer.

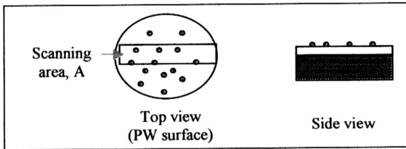

Figure 3.7 (b): Counting area of copper decorated wafer.

3.2.2 Formation of copper dots on oxidized wafer surface

3.2.2.1 Analyzing the purity of anode using Energy Dispersive X-ray Spectroscopy (EDS)

Anode is the source of copper ions for copper dots formation in copper decoration technique. Existing of other metallic elements in the anode might affect the electrolysis process and the shape of copper dots formed on wafer surface. To analyze the composition of anode, a small piece of copper (3 x 3 cm^2) is cut from

analyze the composition of anode, a small piece of copper (3 x 3 cm^2) is cut from the copper plate. Then, it is sent for Energy Dispersive X-ray spectroscopy (EDS, model: S360 Cambridge) to analyze elements of the copper plate.

3.2.2.2 Determination copper concentration in methanol using Inductive Couple Plasma – Optical Emission Spectroscopy (ICP-OES)

During copper decoration, copper ions that dissolved from anode enter methanol and transport to wafer surface. Consequently, it is interesting to study the copper concentration in methanol as a function of time and as a function of magnitude of current. To study copper concentration in methanol with time, the copper decoration unit (anode and teflon container) is first cleaned thoroughly using diluted nitric acid (≈ 1 % volume) to minimize residual copper. The unit is then rinsed with ultra pure deionized water before one liter of methanol (99.99% purity) is poured into the teflon container. Then, an oxidized polished wafer is used for this measurement. The external DC power supply is adjusted to 15V in order to dissolve copper ions into the methanol. One ml of methanol is extracted from the teflon container using a micropipette at time intervals of 0, 15, 30, 45, 60, 75 and 90 minutes after the power is switched on. Each of these samples is then mixed with 99 ml of diluted nitric acid (2% volume) to reduce evaporation and volatility. The copper concentration in the mixture of methanol and HNO_3 solution is measured

using a Perkin Elmer ICP-OES (Model: Optima 3000 XL). The magnitude of current flow through the methanol is recorded at the same time intervals.

On the other hand, to study the effects of magnitude current on copper concentration in methanol, the above procedures are repeated. However, higher voltage, i.e, 25V is used at this time. This is because higher stressed voltage will cause more oxide breakdown and allow more current to flow through the circuit.

3.2.2.3 Detection of permanent damages extended to wafer surface as a result of oxide breakdown

As discussed in section 2.2.2, permanent damages are created on the oxide layer due to oxide breakdown. These damages provide conducting paths through the oxide layer that allowing high current density to flow through it. In this test, these damages can be enlarged for visual inspection using preferential etching (Secco etching).

The samples used are p-type wafers with (100) orientation and resistivity in the range from 8-12 ohm.cm. These oxidized samples are decorated for five minutes at a voltage of 15 volts. Then, small rectangular (around 2mm X 2mm) that enveloping several copper dots is drawn on the surface of the wafer using a diamond tipped pen. These rectangular serve as markers for capturing images on the same surface area. Prior to preferential etching, the copper dots are then removed by dipping the wafer in diluted nitric acid ($\approx$ 1% of volume, 1 minute).

This is followed by removal of the oxide layer by dipping the wafer into diluted hydrofluoric acid (≈ 1% volume, 5minutes). To remove and minimize the amount of particles on the wafer surface, these wafers are then cleaned using standard SC1 solution (H_2O_2: NH4OH: HFW = 1:1:10, 3 minutes). Next, the wafers are Secco etched (potassium: HFW: HF =132.2 gm: 3 L: 6 L, 30 minutes). Finally, microscope images of the same rectangular are taken again. These images are then compared with the previous images.

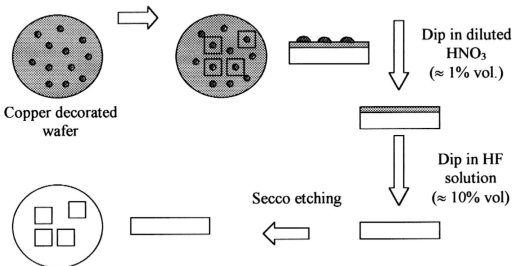

Figure 3.8: Small rectangulars (around 2mm X 2mm) enveloping several copper dots are drawn on the surface of the wafer using a diamond tipped pen. The images of these rectangulars with copper dots are taken. The copper dots are then removed by dipping the wafer in diluted nitric acid. This is followed by removal of the oxide layer by dipping the wafer into diluted hydrofluoric acid. To remove and minimize the amount of particles on the wafer surface, these wafers are then cleaned using standard SC1 solution. Next, the wafers are Secco etched. Finally, microscope images of the same rectangulars are taken again.

3.2.2.4 Studying distribution of copper dots size on copper decorated wafer

It is found that the size and shape of copper dots on copper decorated wafer are different. These might give valuable information to understand the formation of copper dots on wafer surface. A test is carried out on two pieces of wafers to study the distribution of copper dots size and its relationship with the defects of oxide layer. These are P-type wafers, (100) crystal orientation with resistivity range from 9-12 ohm.cm. The oxidized samples are copper decorated at 15V, 5 minutes as discussed in section 3.2.1 (i) – (iii). Then, the distribution of copper dots size (area) on two pieces of copper decorated wafers is determined by using image analyzer (KS400, Carl Zeiss).

To measure the size of copper dots, the pixels of monitor is calibrated with calibration scale at magnification of 50 X by using the image analyzer. This is followed by capturing the images of copper dots at magnification of 50X. The image analyzer analyzes the area of copper dots on the images. For each piece of copper decorated wafers, around 10% of copper dots size is measured. Then, a graph of frequency versus size of copper dots is plotted and analyzed.

3.2.2.5 Studying the impact of size of D-defects on size of copper dots

This test is a continuity of section 3.2.2.4. The purpose of this test is to investigate the relationship between the size of D-defect and size of copper dots. This is

because copper decoration technique is sensitive to D-defects [5, 10, 16, 20, 28-36] at stress field of 5±0.5 MV/cm.

Two pieces of wafers are used in this test. These are P-type wafers, (100) crystal orientation with resistivity range from 9-12 ohm.cm. The oxidized samples are copper decorated at 15V, 5 minutes as discussed in section 3.2.1 (i) – (iii). Then rectangular with size around 5x5 mm^2 are drawn on the copper decorated wafer surface using diamond pen. The images of these rectangular with copper dots are captured using a CCD camera attached to a compound microscope at magnification of 50x. The size of copper dots in each rectangular is measured by image analyzing software (KS400, Carl Zeiss). This is followed by registering the locations of copper dots in each grid using coordinate system of Atomic Force Microscope (Digital Instruments Nanoscope III D5000). Next, the copper dots and SiO_2 film is removed by diluted nitric acid (≈ 1% of volume, 1 minute) and HF solution (≈ 1% volume, 5minutes), respectively. With the coordinate of the locations of copper dots, AFM is used to detect and capture images of the D-defects under the copper dots. The AFM measurement is carried out by using Tapping Mode™, in which the atomic force applied is less than $1x10^{-10}$N. Initially, the scanning area is larger (30µm x 30µm) in order to locate the D-defect. Once the D-defect is detected, it is scanned again with 1µm x 1µm to obtain better resolution of D-defect image. The D-defects size (area) on the scanning image is measured by the image analyzing software again.

3.2.2.6 Effect of stressed field on defect density of copper decorated wafers

The objective of this test is again to study the effects of defects degrade the oxide layer differently. This can be observed by applying different magnitude of stress field to stress the oxide layer. In fact, Shanon [5] has reported that defect density of copper decorated increased with stressed field. This test is repeated by using 3 different crystals. The specification of these crystals is shown in Table 2.

Table 2: Specification of wafers used

Type of wafers	A	B	C
Wafer diameter	6”	6”	8”
Oxygen content (ppma)	16.0 – 20.0	10.5 -12.5	12.5 – 18.7
Resistivity (ohm-cm)	9.0 – 12.0	8.0 –12.0	0.01 – 0.02
Type of dopant	P - type (B)	P – type (B)	P - type (B)

The equipmet and samples of this test are prepared as illustrated in section 3.2.1 (i) – (iii). However, during copper decoration, different applied voltages, starting from 5V, and incremented at 5V intervals until a maximum voltage of 80V are used to stress the oxide layer. Three pieces of wafers from the same type of crystal are decorated for each applied voltage. Besides, the deposition time for each piece of wafer is fixed at 5 minutes. Lastly, the defect density of copper decorated wafers is measured for each applied voltage.

3.2.2.7 Analyzing the composition of grey ring surrounded copper dots by using TOF-SIMS

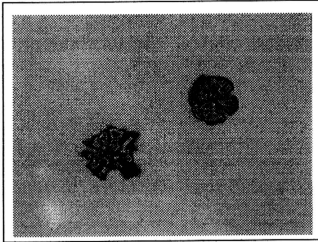

Figure 3.9: Image of copper dots formed on wafer surface observed under 50X optical microscope (plan view). One of the identities of copper dots is that a grey ring surrounds them.

Part of copper ions in the methanol finally will discharge and deposit on wafer surface as copper dots as shown in Fig. 3.9. It is found that the copper dots are surrounded with a grey ring. In fact, this is one of the identities of copper dots, allowing one to distinguish from dust or dirt on wafer surface.

Two pieces of wafers are prepared as discussed in section 3.2.1 (i), (ii) and (iii). These are P-type wafers, (100) crystal orientation with resistivity range from 8-12 ohm-cm. The oxide thickness is 250±10Å. The oxidized samples are copper decorated at 15V, 5 minutes. Then, the composition of the grey black ring is analyzed using TOF-SIMS (Model: TOF-SIMS IV, Cameca). There are two steps in this analysis. Initially, the copper decorated wafers have been analyzed by using secondary ion mass spectra to compare between the mass spectra of copper dot and

reference area (same piece of wafer but do not have copper dot). The scanning area is 500 x 500 μm^2. Mass spectra range is from 0-500. The sampling time is 500 s. When measurement is carried out, the source of primary ion decreases with time. This will affect the counts (intensity) of secondary ion mass spectra. To overcome this problem, the intensity of the secondary ion mass spectra is normalized with the ^{69}Ga intensity (primary ion used for sputtering) for this specific measurement. Then, comparison of intensity between the copper dot area and reference area is carried out. Extra peaks and stronger peaks of mass spectra of the copper dot compared to reference area will be recorded.

The information from above comparison will be used during measurement of secondary ion mass imaging. Similarly, the scanning area is 500 x 500 μm^2 with 500s sampling time in this measurement.

3.2.3 Determination of stressed field by V_{ox} / V_{app} ratio measurement

As illustrated in Fig. 2.1 (a), there is a gap between the wafer surface and anode. This gap is filled with methanol. This results a potential drop across the gap between the copper plate (anode) and the wafer as discussed in section 2.1.3.3. Consequently, the actual voltage (electric field) that stresses the oxide layer (V_{ox}) is lower compared to the applied voltage (V_{app}).

In practice, V_{ox}/V_{app} ratio (m) is measured rather than voltage on the wafer surface (V_{ox}). The V_{ox}/V_{app} ratio (m) needs to be determined in order to calculate the

actual stress field across the oxide layer. The stress field across the oxide layer, E can be obtained from

$$E\left(\frac{MV}{cm}\right) = m\left[\frac{V_{app}}{T_{ox}}\right] \tag{14}$$

where V_{app} is the DC power supply applied voltage, and T_{ox} is the oxide thickness. Since this ratio can provide the user regarding the applied field that stresses the oxide layer corresponding to a particular V_{app}, the effect of voltage probe exposured length on the ratio is studied.

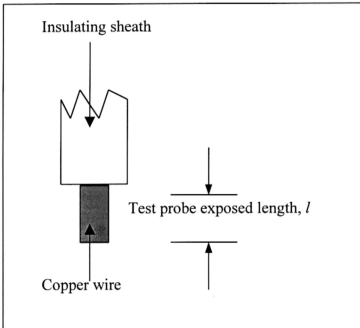

Figure 3.10: Schematic diagram of test probe

To study the effect of voltage probe exposed length, the copper decoration equipment is set up as discussed in section 3.2.1 (i) – (iii). Then, four pieces of

voltage probes (diameter: 0.56mm) with different exposed lengths (l) (as shown in Fig. 3.10) of 0.5, 1.0, 1.5 and 2.0 mm are used. The measurements are simultaneously made at four points near to the center of the wafer surface. Before beginning the measurement, a regular 30 minute seasoning (methanol volume = 1.0 litres, at V_{app} = 15V and limiting current, I = 1.0A) is carried out. The voltage probes are then put in simultaneously to measure the voltage on the wafer surface immediately after the seasoning process. The applied voltage (V_{app}) is gradually ramped up from 3V, at 3V intervals until a maximum of 24V. The respective voltages on the wafer surface (V_{ox}) are then recorded down for each V_{app}. The whole measurement is completed within 30 minutes.

3.2.4 Effects of copper concentration in methanol on copper decoration process

3.2.4.1 Effect of copper concentration on the conductivity of methanol

The impact of copper concentration on conductivity of methanol is studied. The copper decoration unit is cleaned up with diluted nitric acid (≈5% vol.). One liter of methanol is used in the test. Then, one piece of 6" oxidized wafer is loaded into the equipment. A stressed voltage of 15V is applied to the equipment during the copper decoration process. As shown in Fig. 3.11, methanol samples are extracted from the equipment at selected time interval of 0, 15, 30, 45 and 60 min.

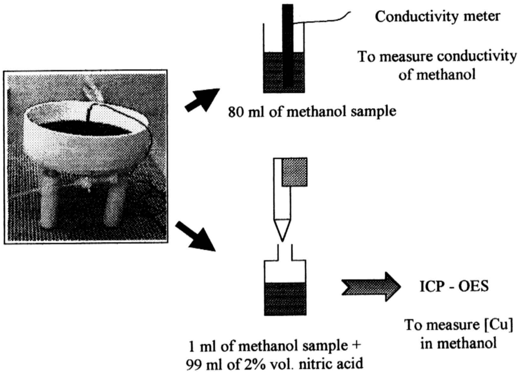

Figure 3.11: The conductivity of methanol is measured by conductivity meter at selected time interval. At the same time, methanol solutions are sampled out from the copper decoration unit. These copper concentrations of the methanol samples are measured by ICP-OES.

Part of the methanol sample is sent to ICP-OES (Model: Optima 3000 XL) for copper concentration measurement. Each sample contains 1ml of methanol sample and 99 ml of 2% vol. diluted acid nitric. On the other hand, conductivity meter (Model: CyberScan CON 500, Eutech Instruments) is used to measure the conductivity of the methanol samples. CyberScan Con 500 meter can automatically compensate for the conductivity change due to temperature at which a solution is being measured. It has measurement accuracy up to ±1% F.S. The meter is calibrated with standard solution 442-15 (11.1 ppm of NaCl, NIST traceable) prior measurement is carried out. In conductivity measurement, 80 ml of methanol is

sampled from the copper decoration unit for each measurement. The probe of conductivity meter is dipped into the polyproplylene container as illustrated in Fig. 3.11. The conductivity of the methanol is recorded after the reading shown in the display of the meter is stable. Then, the methanol samples are poured into the equipment again. The meter probe is rinsed with ultra pure deionized water and dipped into a fresh methanol while waiting for the next measurement.

3.2.4.2 Effect of copper concentration of methanol on the size (average diameter) of copper dots.

As the time increased, the copper concentration in methanol is expected to accumulate during copper decoration. This is because electrolysis process occurs. Since more copper ions are available for deposition, it is interesting to find out the impact of copper concentration on copper dot size.

To investigate the relationship between the copper concentration on the size of the copper dots, twenty-four pieces of p-type wafers, with crystal orientation (100) and resistivity of 9-12 ohm.cm are used. The copper decoration unit and samples are prepared as mentioned in section 3.2.1 (i) – (iii). Each piece of wafers is decorated for 5 minutes at 15V, continuously. Besides, one ml of methanol is extracted from the teflon container using a micropipette at time intervals of 0, 15, 30, 45, 60, 75 and 90 minutes. Each of these samples is then mixed with 99 ml of diluted nitric acid (2% volume) to reduce evaporation and volatility. The copper

concentration in the methanol/ diluted nitric acid samples are measured using a Perkin Elmer ICP-OES (Model: Optima 3000 XL).

Since this test is done before installation of image analyzer (KS 400, Carl Zeiss), the size of copper dots is estimated by averaging the maximum and minimum diameters of the copper dots as given in Fig. 3.12.

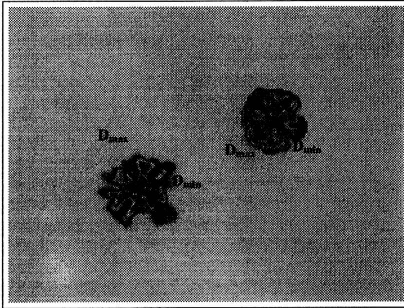

Figure 3.12: Due to the non-uniform shape of the copper dots, the size of the copper dots is estimated by taking the average of the maximum and minimum diameter of the copper dots, i.e. $(D_{max} + D_{min})/2$.

To determine the size of the copper dots at each copper concentration, five copper dots are randomly selected and measured from each piece of wafer.