

# Chapter 2

## Study of suspension stability of Nano-particle with Organic Additive

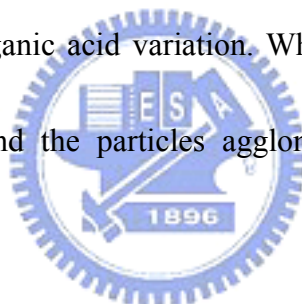
### 2.1 Introduction

Cu CMP was the enable technology for the Damascene processes in the state of the art copper multi-level interconnect IC manufacturing. Slurry for the polishing process played the most important role to control the removal rate, removal non-uniformity and surface finishing of the substrate being polished. In order to minimize substrate damage after polishing, it was necessary to control suspension stability of nano-sized abrasives in aqueous solution for slurry formulation, especially for integration of low mechanical strength of porous low-k dielectric with Cu interconnect. In this study, abrasive suspension would be controlled by adding citric acid, tartaric acid and malonic acid, organic additives for Cu CMP slurry formulation; aggregation of abrasives in aqueous suspension was characterized with acoustic particle size analyzer and its surface charge. Cu surface roughness after polishing with above slurry formulation was characterized by AFM. The relationship between surface damage after polishing and suspension stability was discussed.

## 2.2 Experimental

### 2.2.1 Size and zeta potential measurement

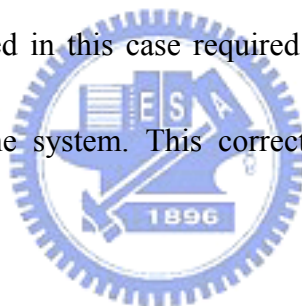
Although the copper film with low hardness coefficient and high extension, the abrasives in the slurry would easily form surface scratch. This research would like to understand the organic acid ions attracting on the abrasives how to change the charges on the surface (electric double layer) that were adjusted the chemicals of the slurry. The best formula would be a stable suspension of abrasives. It also would be less scratches. In this experiment, it would measure the size and the zeta potential of the  $\text{Al}_2\text{O}_3$  abrasives with organic acid variation. While the secondary abrasive size varied, it could be understand the particles agglomeration and the stable of the suspension.



#### **DT-1200 (Zeta-Potential measurement)**

There were two kinds of  $\text{Al}_2\text{O}_3$  abrasive size,  $0.3\mu\text{m}(\alpha)$  and  $0.05\mu\text{m}(\gamma)$ , that were measured by DT-1200, and there were three kinds of organic acids, citric acid, tartaric acid, and malonic acid. Measuring chamber of DT-1200 contained the both acoustic and electroacoustic sensors. As a result this instrument was capable to measure attenuation spectra as well as Colloid Vibration Current. This instrument performed acoustic and electroacoustic measurements separately and independently. At the same time, interpretation software was quite different comparing to the individual

spectrometers. This software provided links between acoustics and electroacoustics. Calculation of Zeta Potential from CVI required information about particle size distribution, acoustic impedance and sound attenuation. ElectroAcoustic Spectrometer DT-300 assumed that particle size was either apriorism known or very small. This assumption made it possible to estimate the acoustic properties of the system. This particle size correction did not work when particle size was unknown from the range above 100 nm. The problem of the particle size correction could be easily resolved when acoustic and electroacoustic spectrometers were combined together. The acoustic spectrometer provided in this case required information about particle size and acoustic properties of the system. This correction was implemented into the DT-1200 software.



## **2.2.2 CMP Process**

### **Wafer preparation**

The blanket Cu test wafers were stacked Cu/Ta layer structure with a combination thickness of 1000/50 nm which were sputtering deposited onto the p-type, (100) oriented, 6-inch bare silicon wafers with 200 nm thick oxide deposited by PECVD.

### **Polisher Setup**

A Westech Model 372M CMP processor (Figure.2-1), consisting of a wafer carrier and a primary circular polishing table mounted with Rodel IC 1400™ grooved (made

of polyurethane impregnated polyester) pad and a secondary buffing table mounted with an Rodel Politex Regular E.<sup>TM</sup> pad, a carrier to hold wafers against the pad, and a Rodel R200-T3 carrier film to provide buff between the carrier and wafer was used for CMP experiments. Recesses in the carrier template mechanically constrain a single 6-inch wafer, preventing it from sliding out from under the carrier during polishing. A polymeric film placed in the recess brought the wafer slightly above the surrounding template surface. When the film was wetted, it provided sufficient surface tension to hold the wafer while it is being positioned over the polishing table.

The teflon retaining ring was recessed from the wafer surface about 7 miles. The slurry, pumped out from a reservoir at a controlled rate, was dispensed onto the center of the table. The table and the carrier were both motor driven spindles, rotated independently at constant angular velocities (rpm). The arm was oscillated about their position at half radius of the table to utilize more pad area and to reduce pad wear [20].

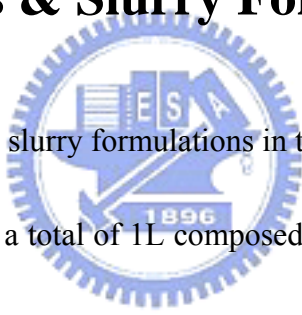
Pressure at the wafer-slurry-pad interface was controlled via an overhead mechanism, which allowed pressure to be applied onto the wafer carrier.

## **Pad Prewet & Pad Conditioning**

Pad prewet was performed before the start of each polishing action. The prewet slurry flow rate was at 300 ml/min and the prewet time was fixed at 20 seconds. Pad

conditioning was employed to resurface the pad in order to maintain the removal rate without sacrificing uniformity. The purpose of pad conditioning was to clean the slurry residuals and to lift the pad fiber for further processing. Without this procedure, the polishing rate decreased substantially after several polishing cycles. In our experiments, pad conditioning was done by brush artificially. Pad conditioning was performed before and between each wafer, and polishing was terminated before pad glazing could cause significant reduction in removal rate.

## Polishing Recipes & Slurry Formations



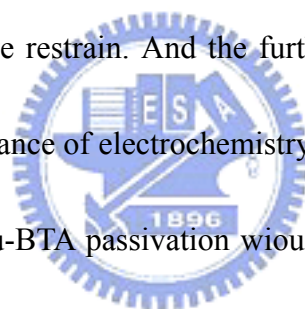
The polishing recipes and slurry formulations in this experiment were all listed in the table.2-3. The slurries was a total of 1L composed of 1%HNO<sub>3</sub> · 0.01M organic acid · 1%Al<sub>2</sub>O<sub>3</sub> and DI water. In the phase1, oxide layers were polished to establish the fresher surface and would bond with Cu ions easily. Phase2 is to remove the residual slurry from wafer surface.

### Buffing step

After polishing, buffing with HNO<sub>3</sub>/1H-BTA was used to remove colloidal silica. Blank wafers were dry spun at the rotation rate of 2500 rpm following buffing. The buffing recipe was listed

### The inhibitor BTA (Benzotriazole)

BTA was that one kind was utilized anticorrosive inhibitor suppressing the metal to etch extensively, that recorded in accordance with other research documents [16][17], BTA could be dissolved under the acid environment, and if when the copper metal surface etched does not have any metal oxide (namely the clean copper metal surface), then BTA would be made use of the anticorrosive passivation layer that the way to shut by mistake formed Cu-BTA in copper metal surface and inferior copper. It could be an know [18][19], when BTA was added in the nitric acid aqueous solution by Tafel picture of electric chemical analysis, copper corrosion, metal of surface electric current could effective restrain. And the further one was examined with the quantity of exchanging impedance of electrochemistry, when BTA thickness increased, the impedance on story of Cu-BTA passivation would become lareger, and then the passivation (Inner) of making copper metal surface and changing, It was relatively difficult that this would make copper oxidized by the nitric acid. Cu-BTA was a anticorrosive passivation layer, so it was a mono-molecular layer. Impedance of Cu-BTA passivation layer became larger that resulted from BTA molecule on the copper surface arranged denser.



## **AFM Analysis**

In order to evaluate the practicability of  $\text{HNO}_3/\text{BTA}$  buffing and  $\text{KOH}$  buffing for removing colloidal silica abrasives on the polished Cu surface, atomic force

microscope (AFM) was employed to scould a  $5\mu\text{m}\times 5\mu\text{m}$  area of Cu surface. In AFM, a fine tip scouldning on the substrate measured surface morphology and properties through an interaction between the tip and surface. In the used measuring mode commonly, the distance between the tip and sample surface was kept constant by a feedback loop during the measurements. There were three operation modes of the AFM (Digital Instruments DI 5000) used to measure the SAM surface quality. From the image resolution viewpoint, contact mode scanning was the best but it would damage the sample surface. Hence, the tapping mode scanning of the AFM was used to measure the surface morphology in this study.

## **2.3 Results and discussions**

### **2.3.1 Titration in the neutral slurry**

We used the neutral slurry in this experiment, that the electrochemical analysis could understand the corrosive behaviors of copper (figure 2-2) [4]. While malonic acid used as oxidizer, that the pH of the solution above  $\text{pH}=3.8$ , the corrosion behavior of copper in this solution was a simple dissolution. While the pH above  $\text{pH}=7$  ( Cu pourbaix diagram fig 2-3), that the surface of copper would produce copper oxide and copper di-oxide, it would be two different copper CMP mechanism. Therefore, the pH of using neutral slurry as far as manipulated in the weak acid condition.

In the weak acid condition, the organic acids would affect the secondary particle size of aluminum oxide ( $\text{Al}_2\text{O}_3$ ). While each of the organic acid was used as oxidizer, although the slurry content would be the same aluminum oxide abrasive, pH of the slurry all fixed in about  $\text{pH}=4$  ( table 2-1 and figure 2-4). The IEP of the abrasive would be altered since the different solution formed the different surface electrical double layer, and then the different slurry would be different IEP. Besides, abrasive of different composition of slurry would form different EDL on the surface of abrasive. The zeta-potential of the abrasive would be altered that the abrasive in the approximate pH of slurry would be different secondary particle size.

The titration was measured by DT1200 shown in fig 2-5 to fig 2-10. The slurry composed of 0.01M three organic acids and two particle size (0.3 $\mu\text{m}$  and 0.05 $\mu\text{m}$ ) aluminum oxides, and then the IEP of these slurries would be shown in table 2-2.

### **2.3.2 Surface morphology after buffing**

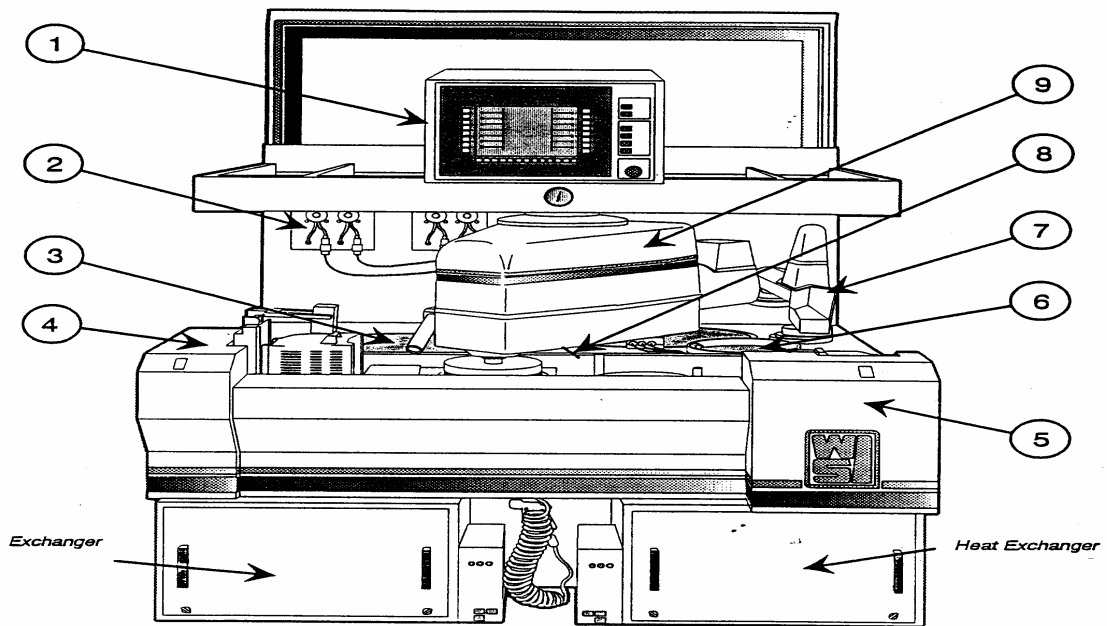
To build the condition of Cu oxide on Cu surface to describe the surface condition after conventional CMP, KOH was used for buffing in this study. AFM was used to characterize the surface morphology after buffing to check if buffing with KOH remove colloidal silica or not. The AFM analysis of buffing with  $\text{HNO}_3$ /1H-BTA showed in Fig 2-11 to Fig 2-16. As shown, a clean Cu surface was observed after buffing with  $\text{HNO}_3$ /1H-BTA, which agreed with the result in the thesis



of Po-Lin Chen [3]. As shown, buffing with KOH could remove colloidal silica. However, the concentration of KOH and polishing time of buffing would dramatically influence the roughness of polished Cu surface. Buffing with 1M KOH for 1 minutes could bring about the cleanest surface and the least roughness.

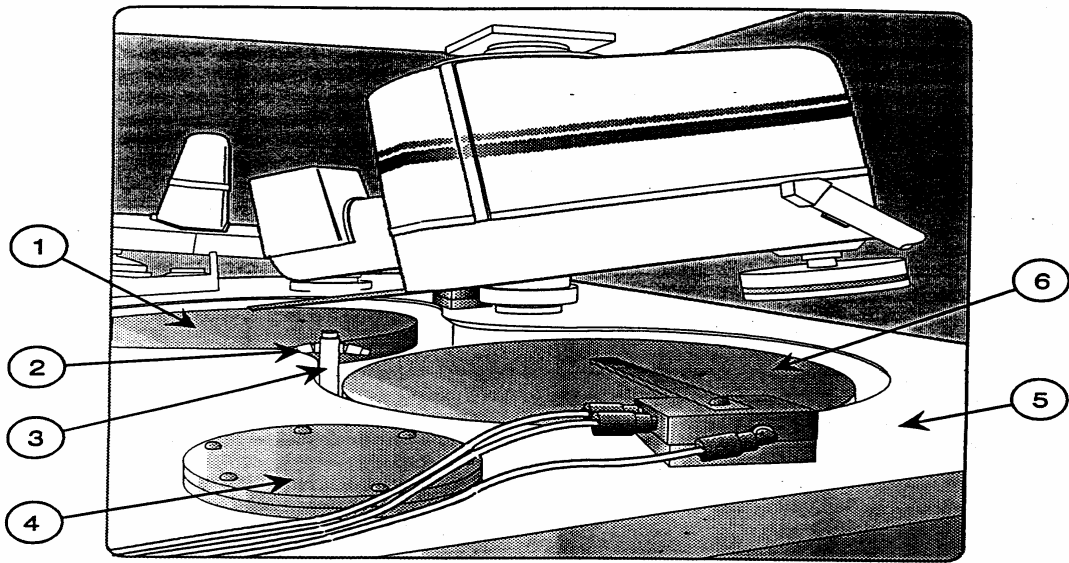
## 2.4 Summary

In the neutral slurry, the corrosive behavior of copper in the neutral condition would be easily affected by pH, so there were two different corrosive behaviors. Therefore, the composition of slurry as far as controlled in the weak acid condition. Different organic acids would be used as oxidizer in the slurry, although the slurry contained the same colloidal aluminum oxide and the pH of the slurry would be fixed at pH=4, but the IEP of the abrasive would be changed because the abrasives in the different slurry formed different EDL on the surface of the abrasives, and then the abrasives in the different slurry would be different IEP and secondary particle size.



- |                                  |                                    |
|----------------------------------|------------------------------------|
| 1 - Control Console & Overarm    | 6 - Clean Station & Slurry Primary |
| 2 - Slurry Motors & Slurry Final | 7 - Rotating Pad Conditioner II    |
| 3 - Platens and Drains           | 8 - Polish Arm Drive               |
| 4 - Unload Station               | 9 - Polish Arm                     |
| 5 - Load Station                 | - Heat Exchanger                   |

Figure.2-1 (a) Schematic diagram of the Westtech Model 327M CMP polisher  
 (b) Platen assemblies of the Westtech Model 327M CMP polisher.



- 1 - Primary Platen, Cooled (372-21110)
- 2 - Spray Nozzle (372M-44160)
- 3 - Spray Tube (372M-44160)
- 4 - Pad Conditioner Cover (372M-44160)
- 5 - Contour Top (372M-44160)
- 6 - Final Platen, Cooled (372-21111)

Figure.2-1 (a) Schematic diagram of the Westtech Model 327M CMP polisher  
 (b) Platen assemblies of the Westtech Model 327M CMP polisher.



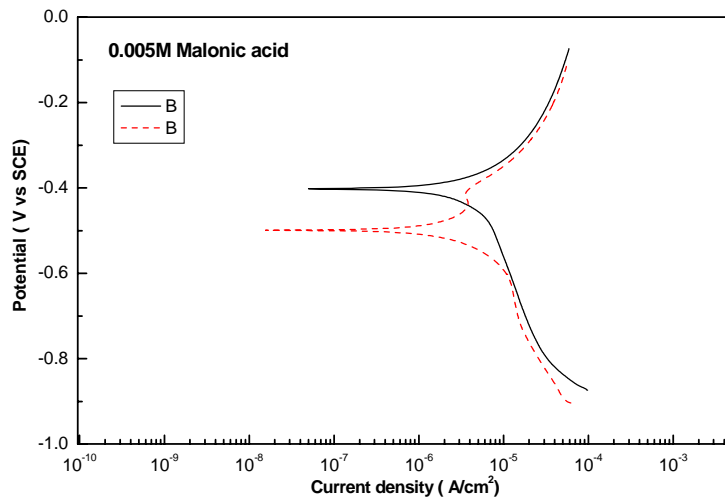


Figure 2-2 Tafel plot of copper corrosion in malonic acid

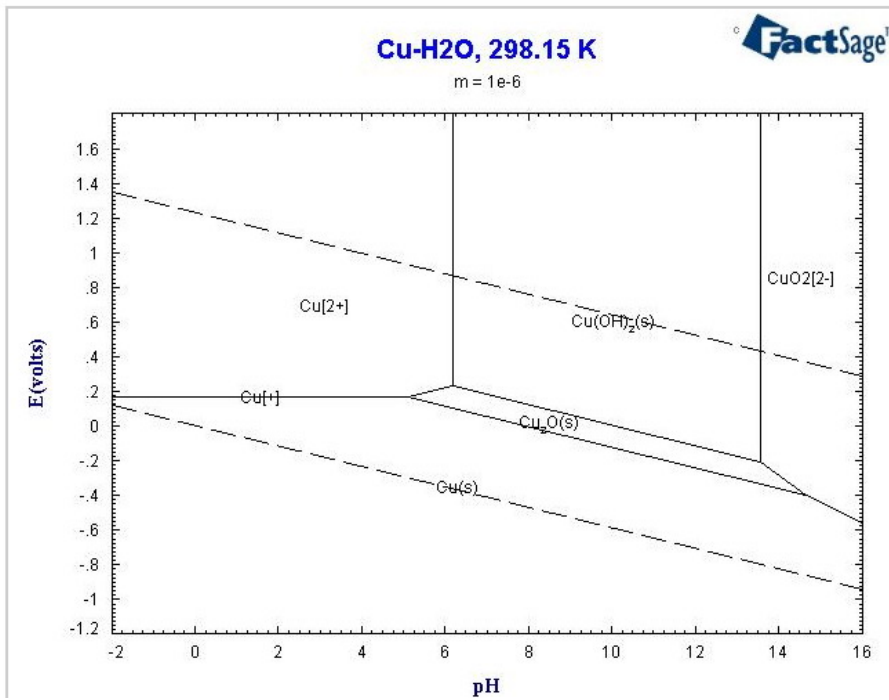


Figure 2-3 Copper pourbaix diagram

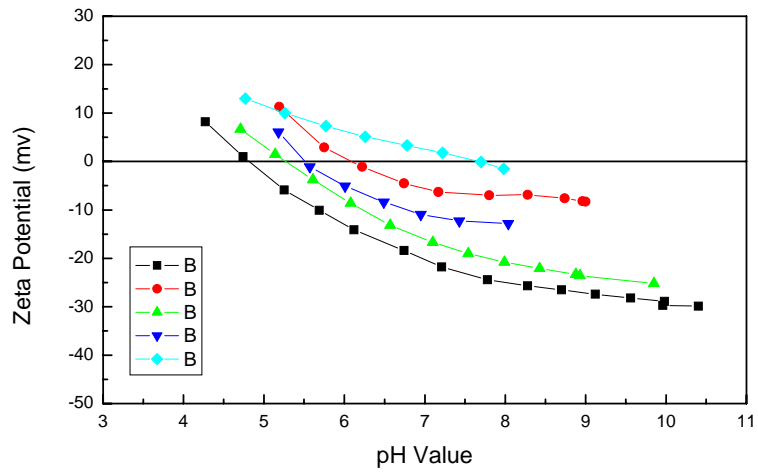


Figure 2-4 Zeta potential of alumina abrasives in neutral solution with ionic carboxylic acid



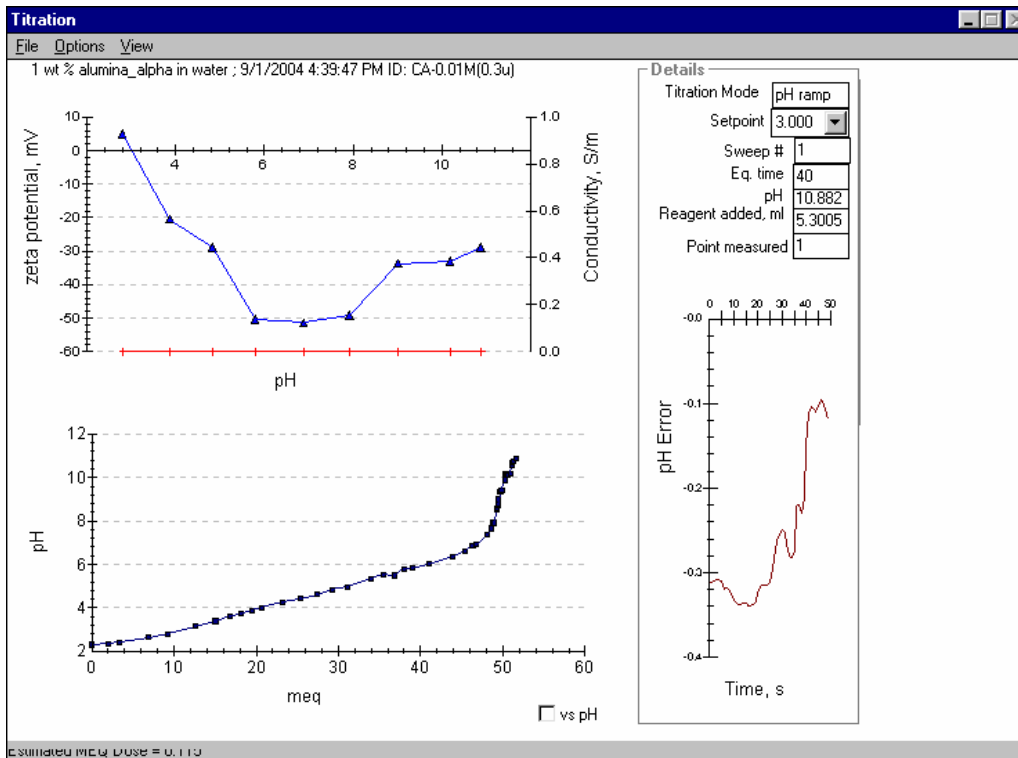


Figure 2-5 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.3 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M Citric acid additive.

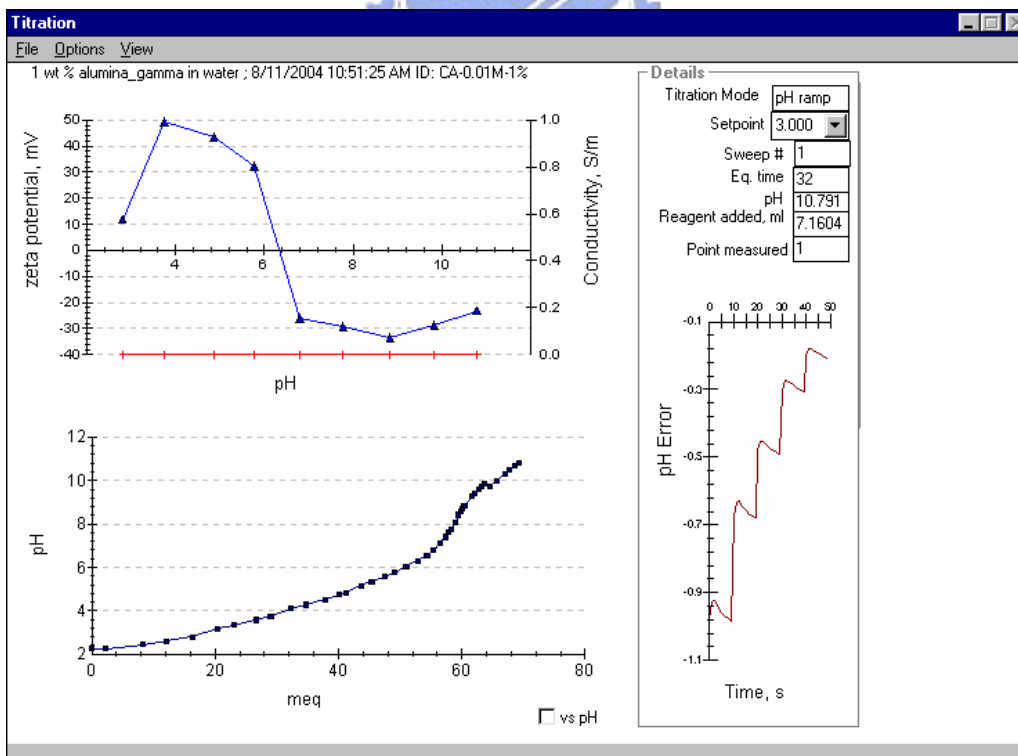


Figure 2-6 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.05 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M Citric acid additive

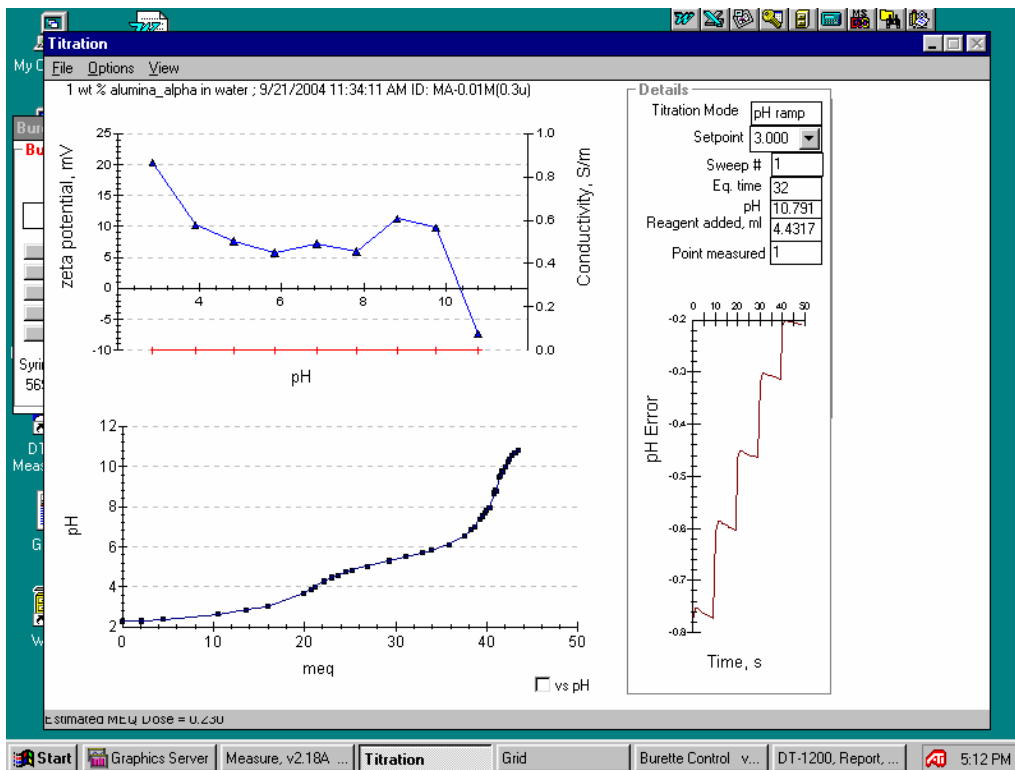


Figure 2-7 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.3 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M malonic acid additive.

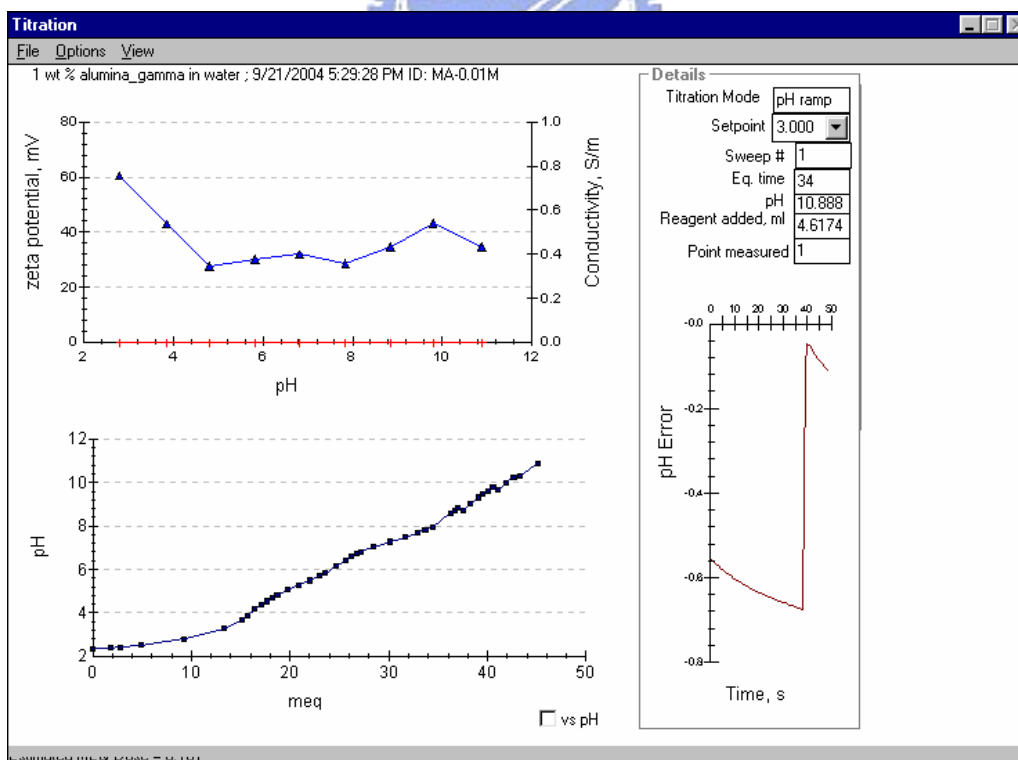


Figure 2-8 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.05 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M malonic acid additive.

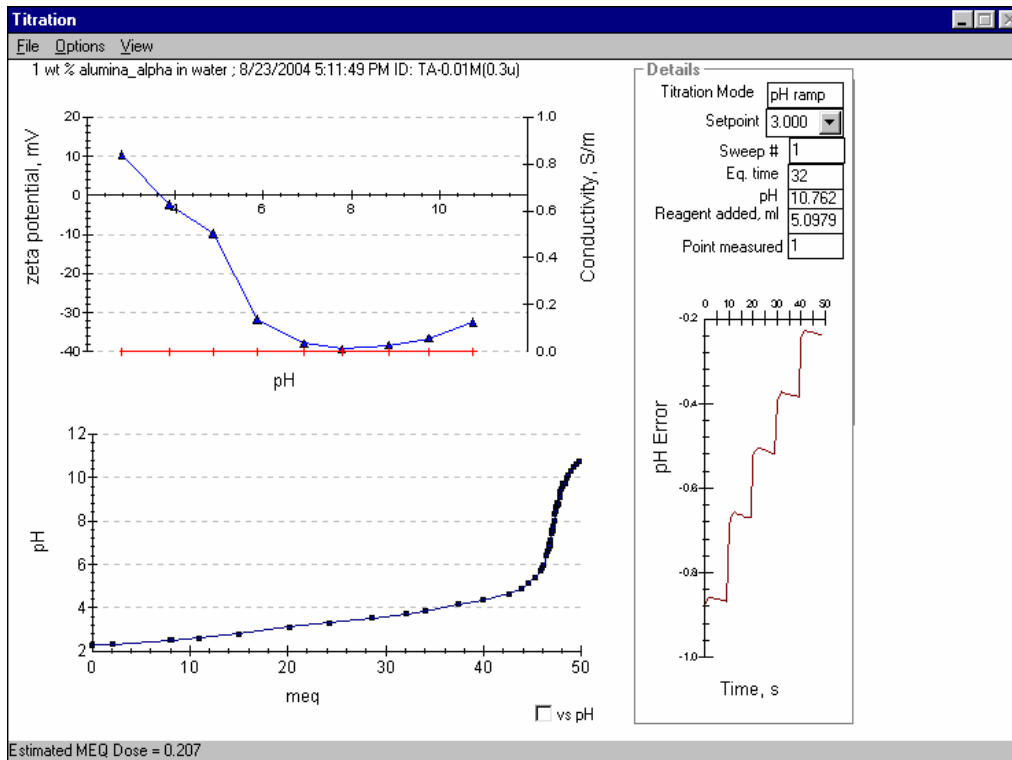


Figure. 2-9 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.3 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M tataric acid additive.

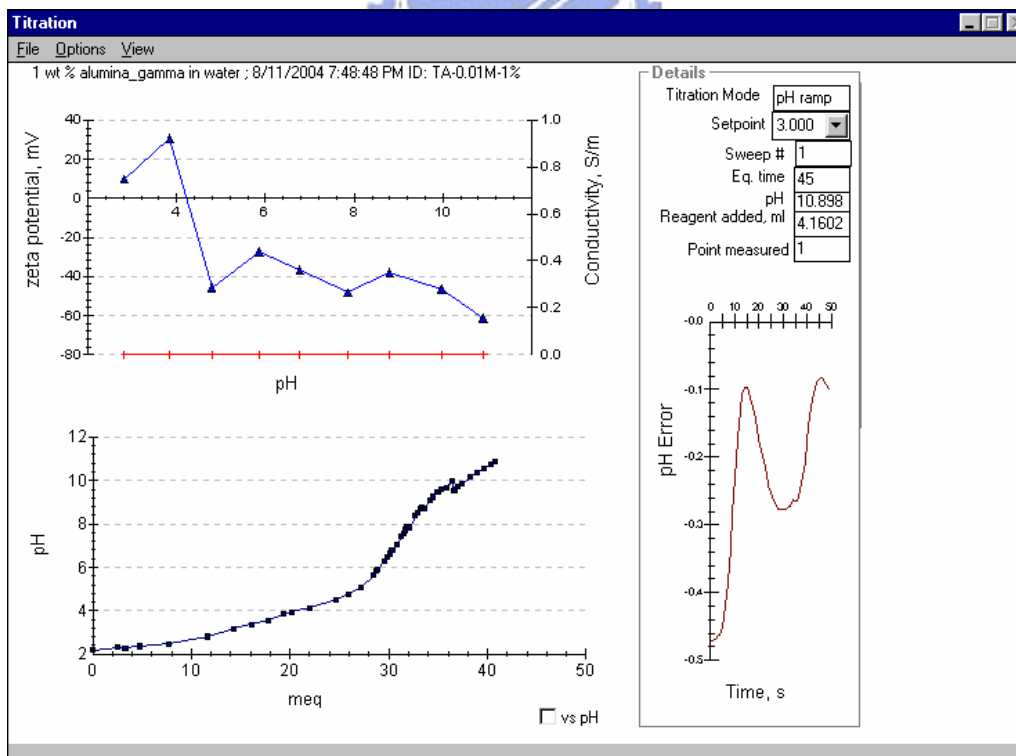
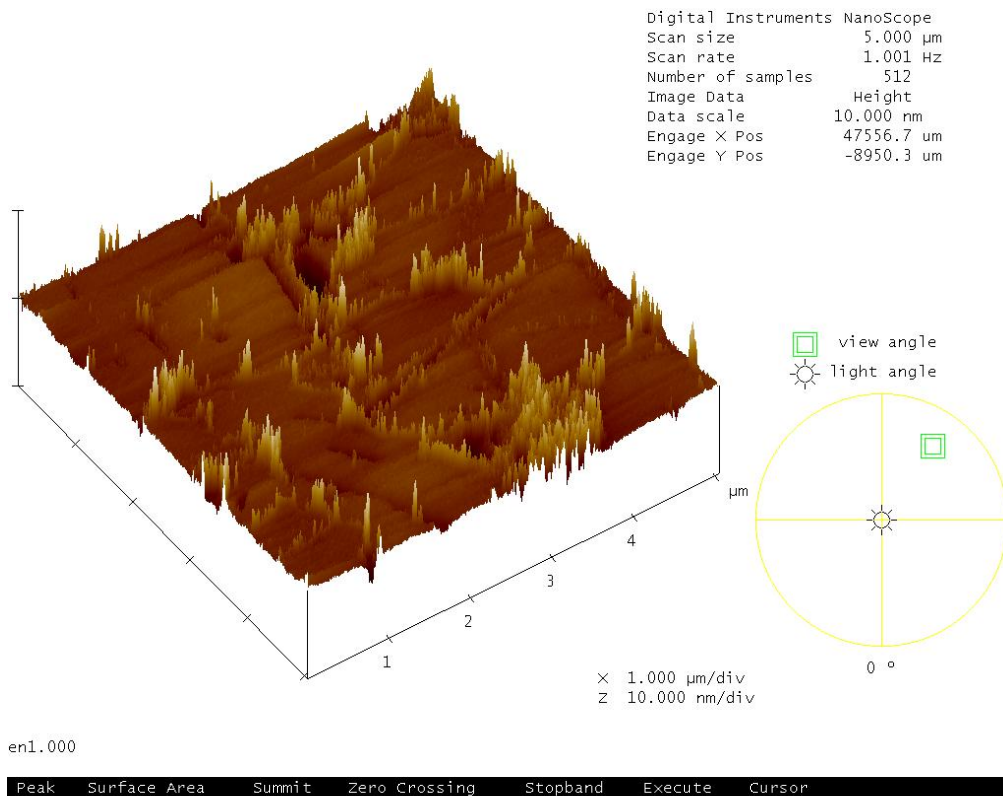


Figure. 2-10 Zeta potential & 2<sup>nd</sup> particle size distribution of 0.05 $\mu$  Al<sub>2</sub>O<sub>3</sub> aqueous suspension with 0.01M tataric acid additive.





### Roughness Analysis

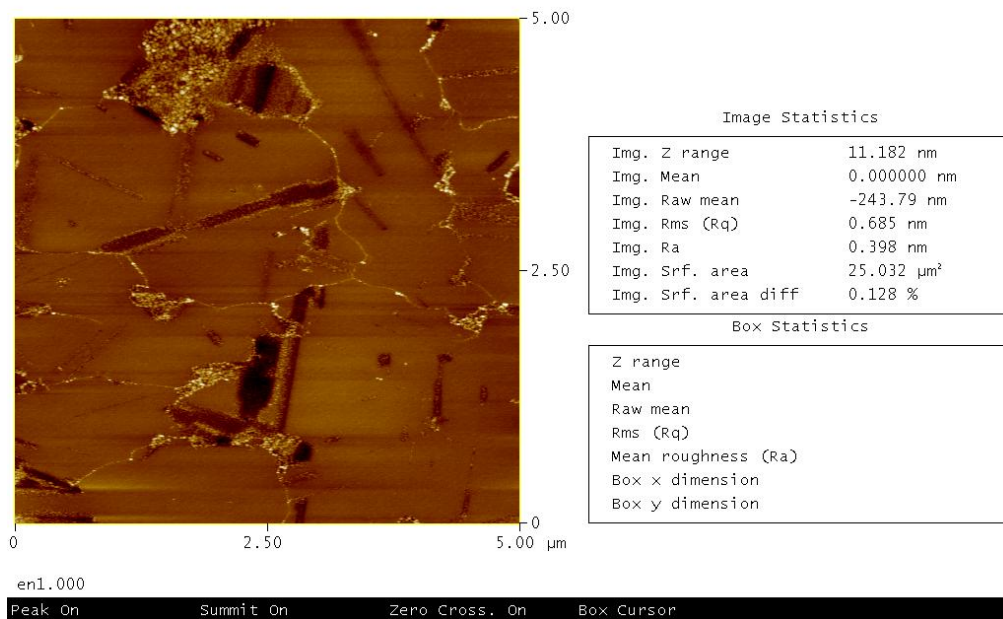
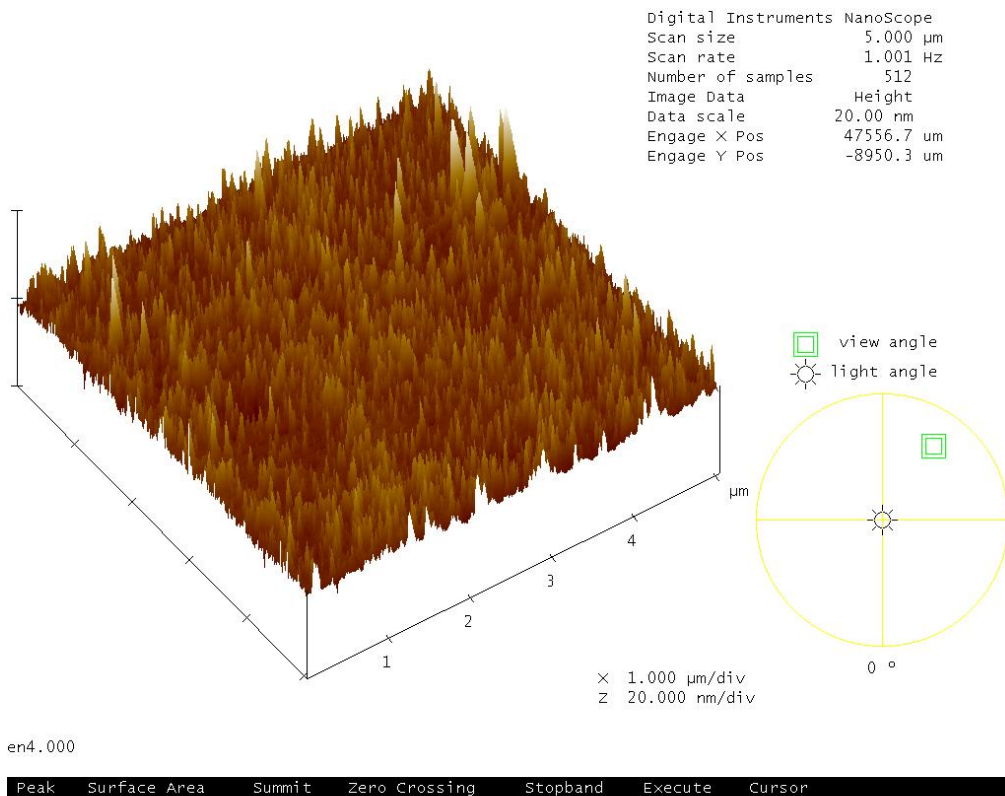


Figure 2-11 Polished Cu AFM ( $0.3\mu\text{Al}_2\text{O}_3$ , 0.01M Citric acid)



### Roughness Analysis

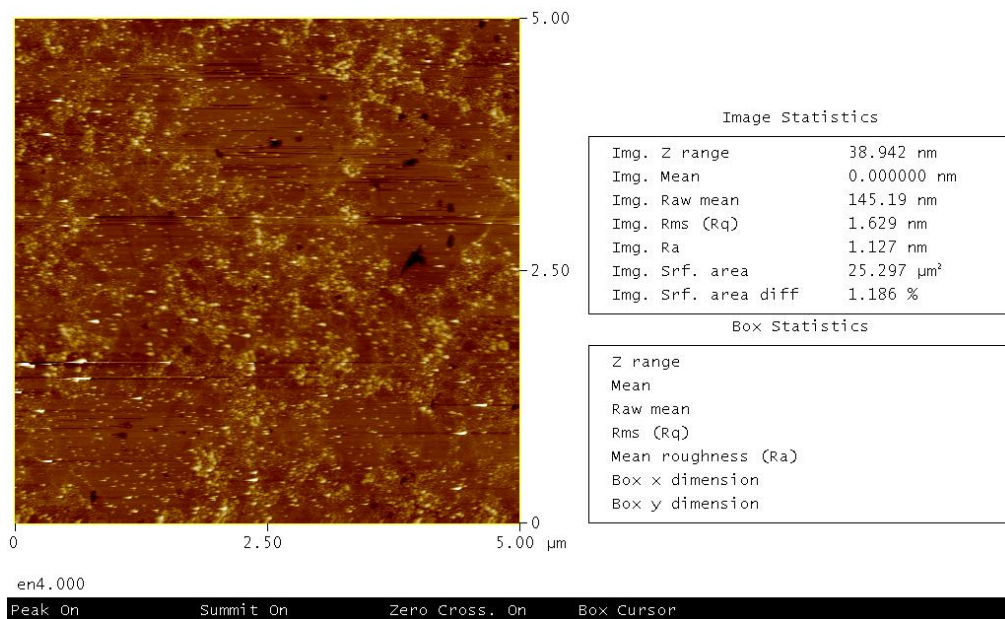
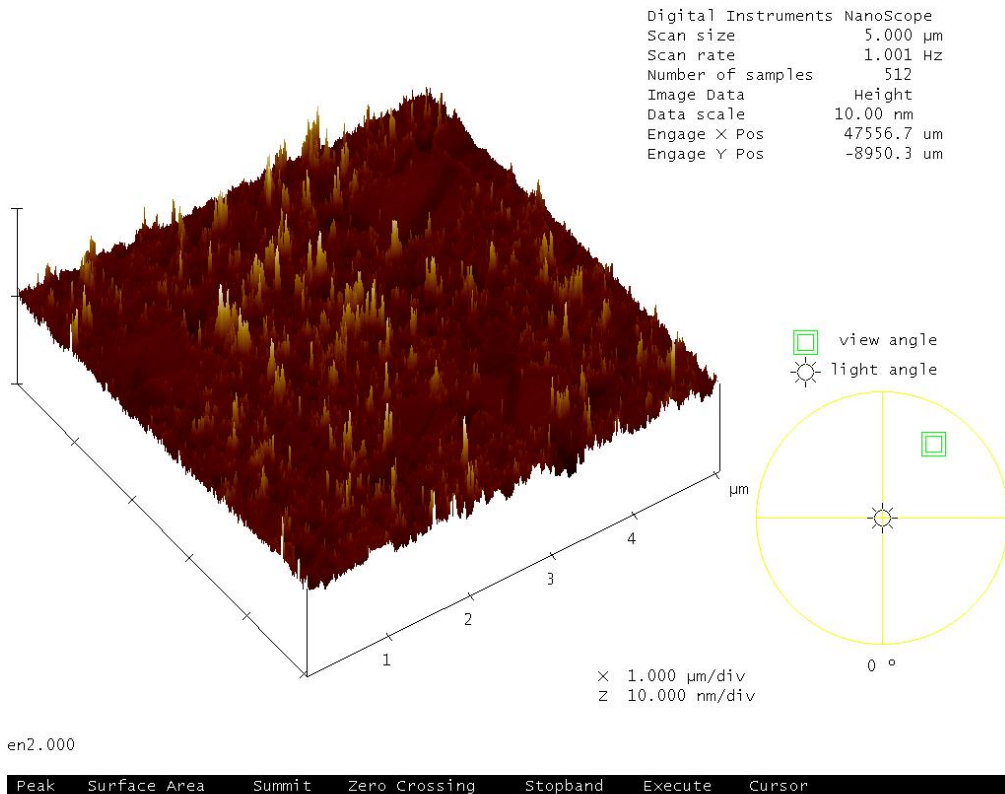


Figure. 2-12 Polished Cu AFM (0.05 $\mu\text{m}$   $\text{Al}_2\text{O}_3$ , 0.01M Citric acid)



Roughness Analysis

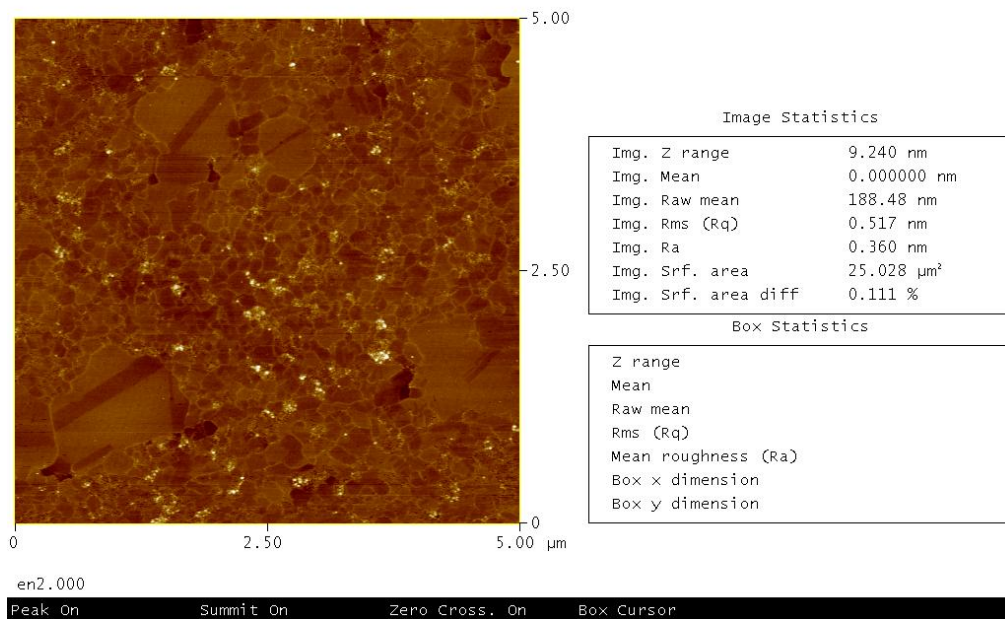
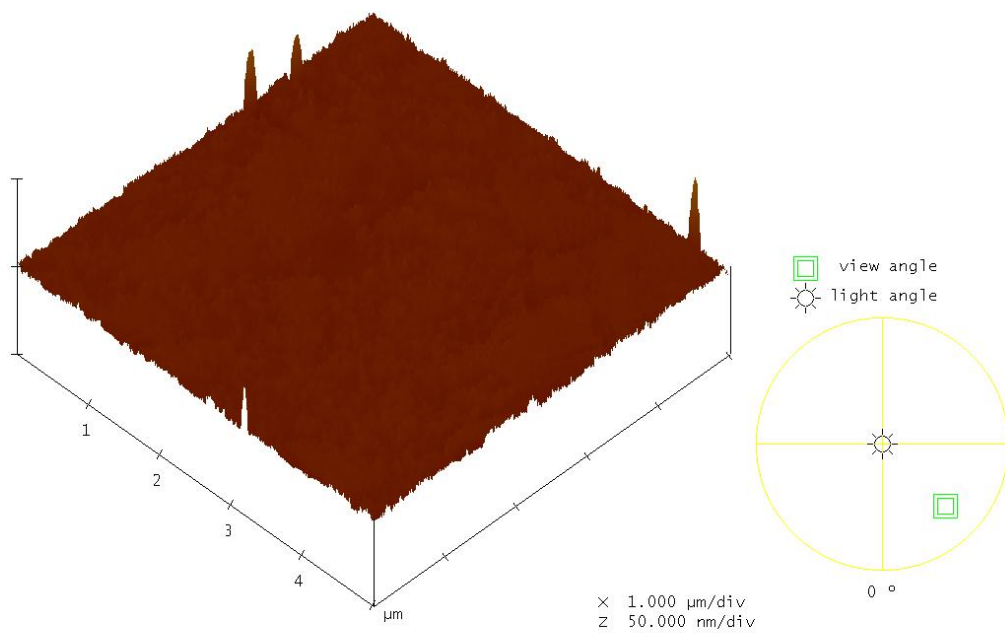


Figure. 2-13 Polished Cu AFM ( $0.3\mu\text{ Al}_2\text{O}_3$ , 0.01M Malnoic acid)



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor

### Roughness Analysis

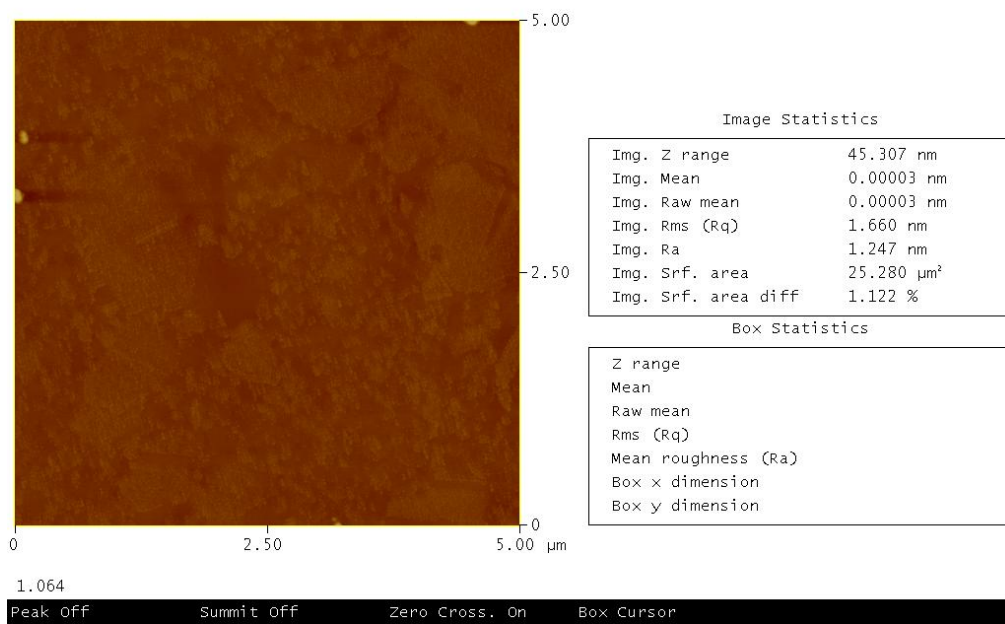
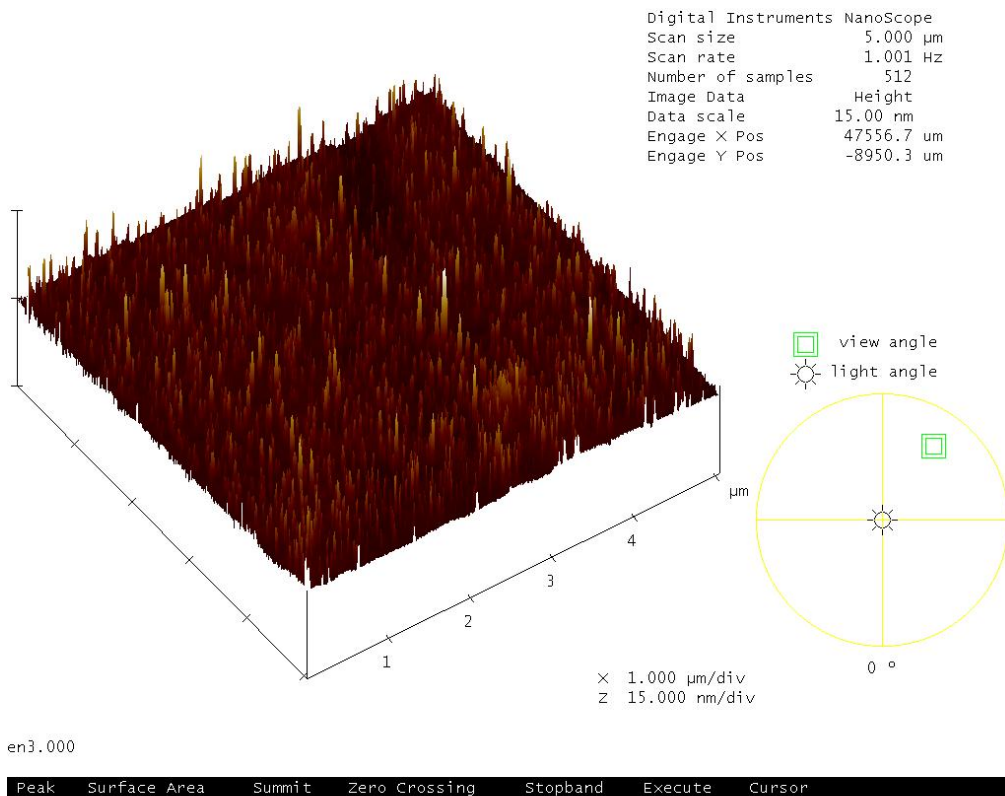


Figure. 2-14 Polished Cu AFM (0.05μ Al<sub>2</sub>O<sub>3</sub>, 0.01M Malnoic acid)



### Roughness Analysis

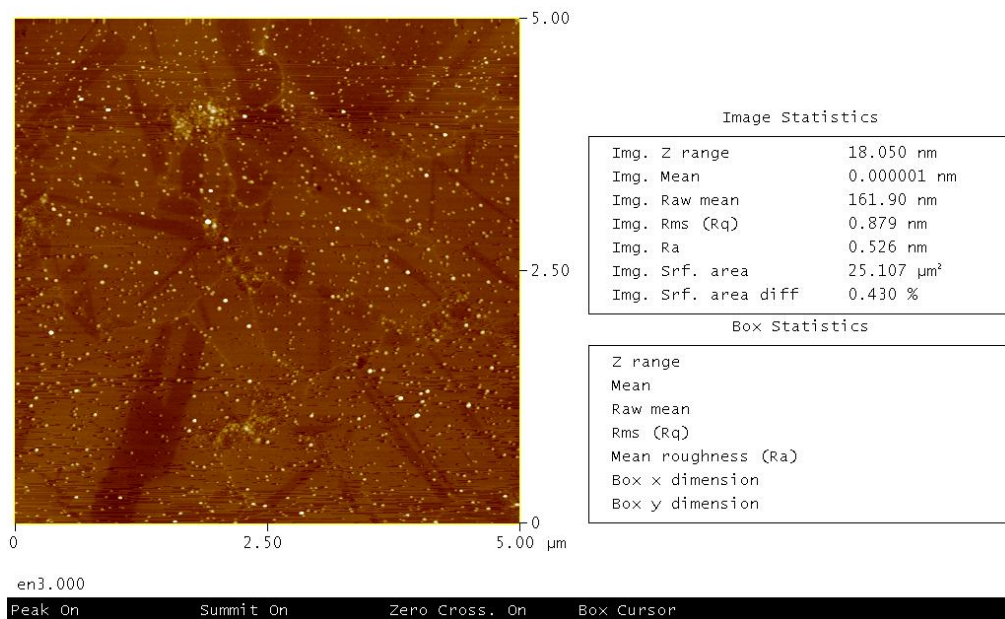
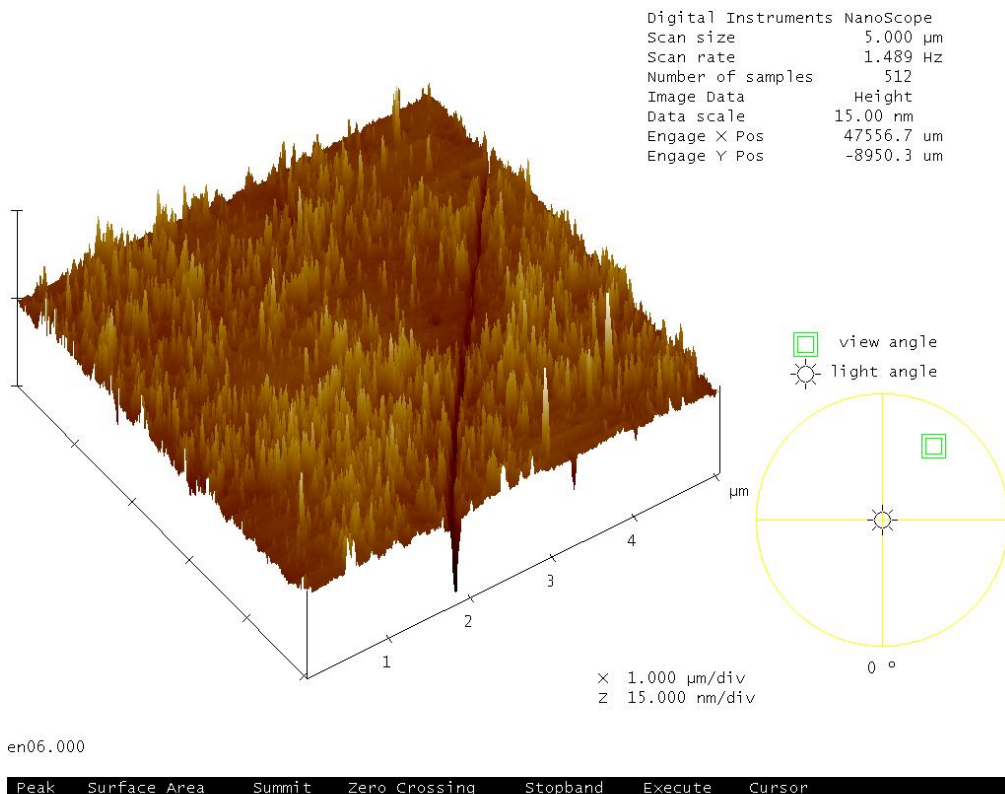


Figure 2-15 Polished Cu AFM ( $0.3\mu\text{ Al}_2\text{O}_3$ , 0.01M Tataric acid)



Roughness Analysis

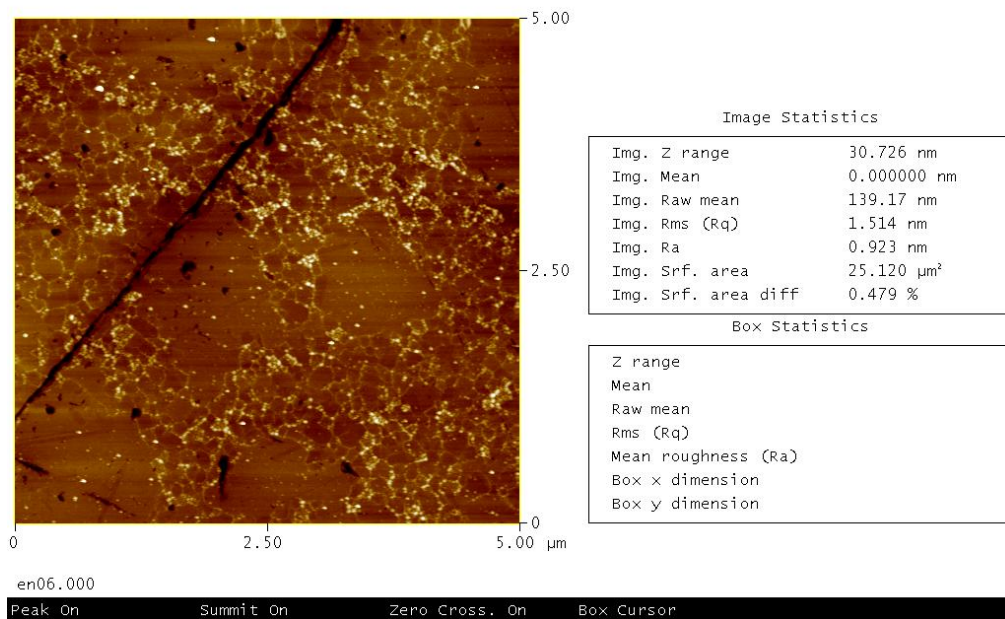


Figure 2-16 Polished Cu AFM ( $0.05\mu\text{Al}_2\text{O}_3$ , 0.01M Tataric acid)

Clean solu	Citric	Malonic	Tartaric	Oxalic	EDTA
D50(nm)	636	213	320	341	72.1
Zeta(mv)	10.9	13.6	7.92	7.34	<b>28.5</b>
<b>pH</b>	<b>3.79</b>	<b>4.89</b>	<b>4.03</b>	<b>4.79</b>	<b>4.18</b>
<b>IEP</b>	<b>4.75</b>	<b>6.1</b>	<b>4.75</b>	<b>5.52</b>	<b>7.7</b>

Table 2-1 Zeta potential of alumina abrasives in neutral solution with ionic carboxylic acids

Composition	0.3um & 0.01M citric acid	0.05um & 0.01M citric acid	0.3um & 0.01M malonic acid	0.05um & 0.01M malonic acid	0.3um & 0.01M tartaric acid	0.05um & 0.01M tartaric acid
IEP	3	6.4	10.4	>11	3.6	4.2

Table 2-2 IEP of different composed slurry

	<b>Primary</b>	<b>Final</b>	<b>Buffing(Final)</b>
Down force	3.0 psi	1.5 psi	5.0 psi
Back pressure	1.5psi	0 psi	2.0 psi
Platen/carrier speed	25/30pm	20/25 rpm	42/45 rpm
Slurry flow rate	150 ml/min	150 ml/min	150 ml/min
Temperature	27 °C	27 °C	27 °C
Polishing Pad	Rodel Politex Regular E.™		
Carrier Film	Rodel R200 T3		
Slurry formulation	parameter	DIW	HNO <sub>3</sub> /BTA=3%/1E <sup>-4</sup> M
Polish time	1min	30sec	1min

Table.2-3 Polishing parameters for surface morphology evaluation.