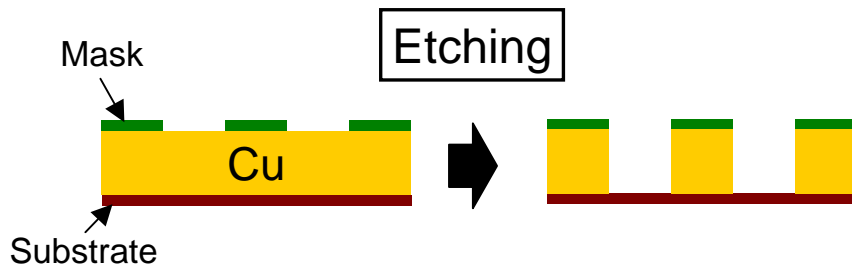


● Introduction

The etching is used to remove the conductor for the wiring-pattern of the print wiring board. The wet etching is superior to dry etching in mass productivity and the cost though it is inferior in the miniaturization. The etching rate and the etched morphology depend strongly on the composition of etching solution.



Problems of the wet etching

... bad microfabrication

Undercut

➡ Etching that advances in the side direction.

Dry etching method

gas, plasma , beam etc. system

... good microfabrication / using expensive devices



Wet etching method

solution system

... excellent mass productivity, low cost

In the present study, etching reactions are investigated by electrochemical methods on the basis of mixed potential theory.

Theory

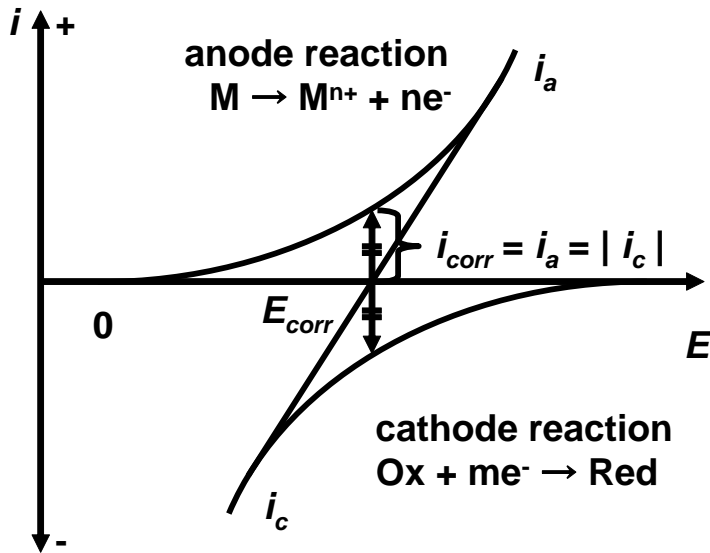


Fig. Scheme of polarization curves at the mixed potential

Anodic reaction of the metal dissolution

+

Cathodic reaction of an oxidant



Mixed potential

➡ Corrosion potential = Etching potential

Addition of oxidant

➡ Corrosion potential and dissolution rate are decided.

The cathode reaction of the oxidant is simulated by imposing electrode potential.

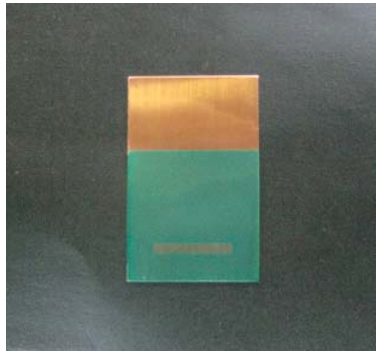


We analyzed copper etching mechanism depending on electrode potential.

● Fabrication of working electrode

The resist pattern for micro-wiring was printed on the copper sheet by screen-printing.

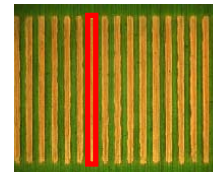
The copper sheet was masked by insulating resin.



10 mm

Fig. Photograph of the copper sheet working electrode

Copper sheet
↓
Acid washing
↓
Water washing
↓
Screen-printing
↓
Drying (120 °C, 30 min)



1.0 mm

Fig. Zoom-in

Rectangular cavities

Width: 80 μm , Length: 2 mm

Distance: 100 μm

Number of cavities: 80

Polarization curves

The polarization curves of the copper electrode were measured in 0.2 M HCl + 1.0 M NH₄Cl.

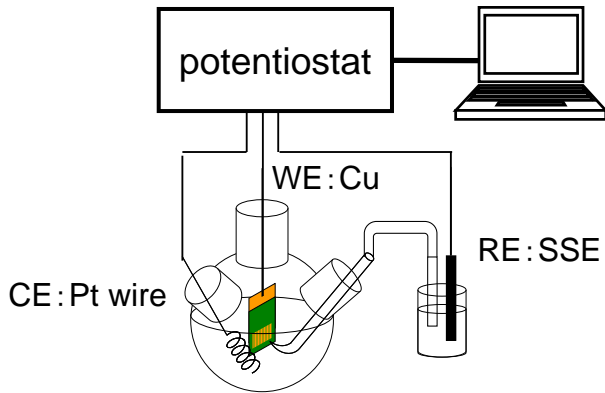


Fig. Scheme of experimental apparatus

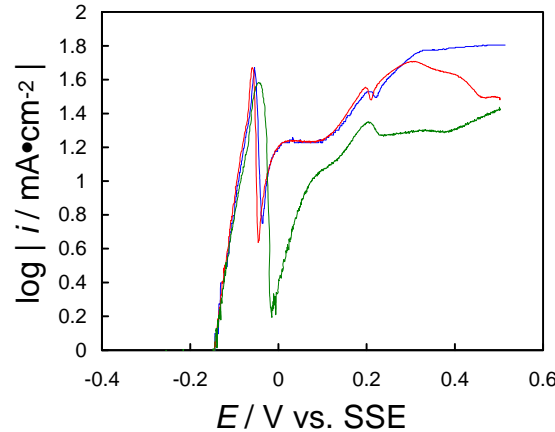


Fig. Anode polarization curve of copper in 0.2 M HCl + 1 M NH₄Cl solution

- Sweep rate : 100 mV / min
- Cu sheet electrode
- Cu film electrode (thickness: 8 μm)
- Cu disk electrode (φ 5 mm)

The polarization curve is divided into three distinct potential regions on the basis of dissolution mechanism of copper²⁾.

Typical cupric chloride etchant¹⁾

composition	
CuCl ₂ ·2H ₂ O	0.5~2.5 M ← oxidant
HCl	0.2~0.6 M
NH ₄ Cl	2.4~0.5 M
H ₂ O	*

1) W.Thurmal, U.S.Patent 3, 306, 792 (1963).



Solution without oxidant

0.2 M HCl + 1.0 M NH₄Cl

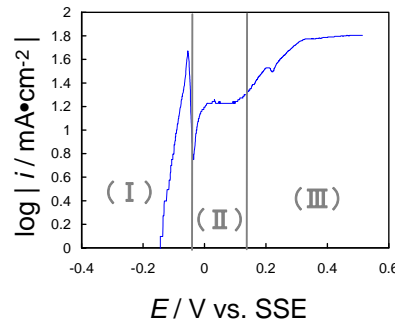
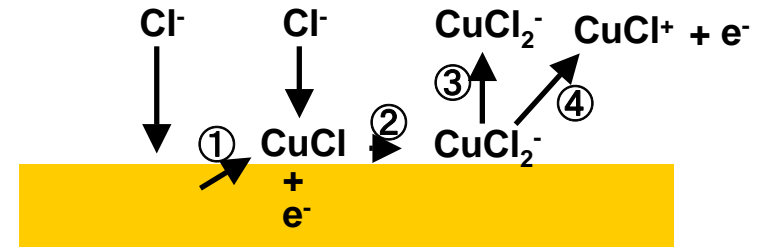


Fig. Anode polarization curve



- ① $\text{Cu} + \text{Cl}^- \rightleftharpoons \text{CuCl}_{\text{ad}} + \text{e}^-$
 - ② $\text{CuCl}_{\text{ad}} + \text{Cl}^- \rightleftharpoons \text{CuCl}_2^{\text{surf}}$
 - ③ $\text{CuCl}_2^{\text{surf}} \rightleftharpoons \text{CuCl}_2^{\text{bulk}}$
 - ④ $\text{CuCl}_2^{\text{surf}} \rightleftharpoons \text{CuCl}^+ + \text{Cl}^- + \text{e}^-$ — Region (III)
- Region (I) (II) (III)

Fig. Cu of dissolution mechanism²⁾

● Potentiostatic measurement

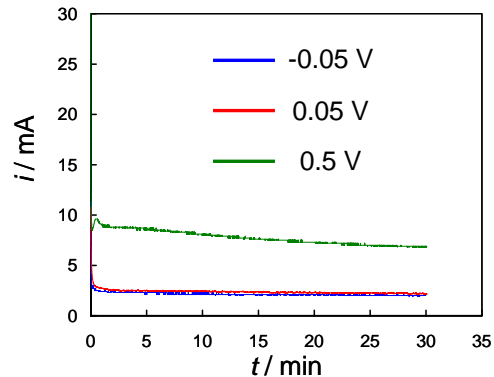


Fig. Current-time curves
(in 0.2 M HCl + 1.0 M NH_4Cl)

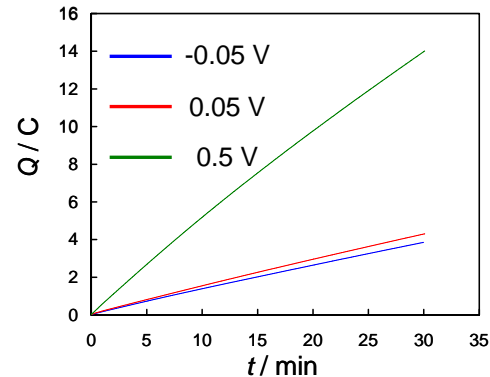
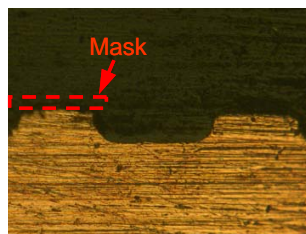
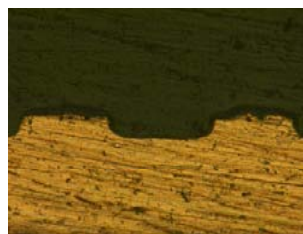


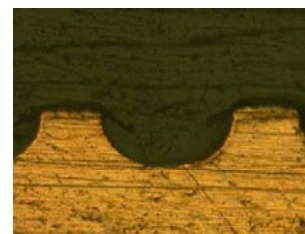
Fig. Charge-time curves
(in 0.2 M HCl + 1.0 M NH_4Cl)



(a) -0.05 V vs. SSE



(b) 0.05 V vs. SSE



(c) 0.5 V vs. SSE

Fig. The cross-section of the electrode observed by optical microscope.

Etched electrodes were cast in epoxy and cut.
Then the cross-sections were polished by 0.05 μm alumina powder.

• The valence in the metal dissolution was calculated by the charge.

The calculation of the valence

Faraday's law : $Q = \frac{m n F}{M_{Cu}}$

$F = 96485 [C]$

$M_{Cu} = 63.536$

$m = \text{volume} \cdot r_{Cu}$

$r_{Cu} = 8920 \text{ kg} / \text{m}^3$

$\text{volume} = \text{Length} \cdot \text{width} \cdot \text{depth} \cdot 80$

Potential E V vs. SSE	Width μm	Depth μm
-0.05	110	30
0.5	125	60

• -0.05 V (30 min)

• 0.5 V (30 min)

$Q = 3.9$, $m = 2.35$ [mg]

$Q = 14$, $m = 5.35$ [mg]

$\therefore n = 1.09$

$\therefore n = 1.72$

.....
The copper dissolution of 2 values results at 0.5 V.

Electrode potential was held until integration charge Q reached 6.5 C.

• Potential: -0.05, 0.5 V

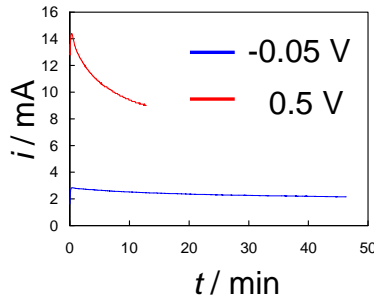
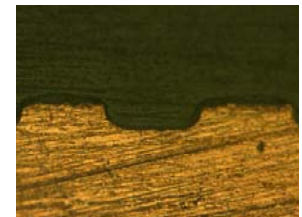


Fig. Current-time curves (in 0.2 M HCl + 1.0 M NH₄Cl)



100 μm

(a) -0.05 V vs. SSE



100 μm

(b) 0.5 V vs. SSE

Fig. The cross-section of the electrode

Immersion potential measurement

The immersion potential measured in solution containing oxidant.

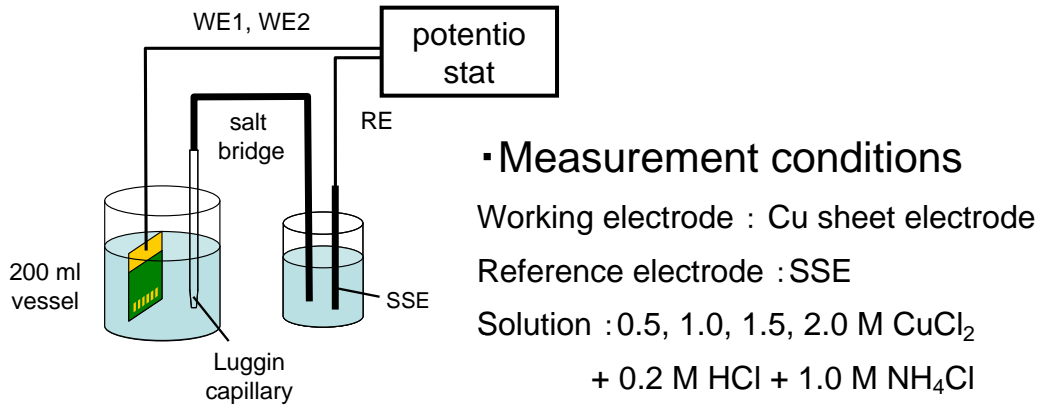


Fig. Scheme of experimental apparatus

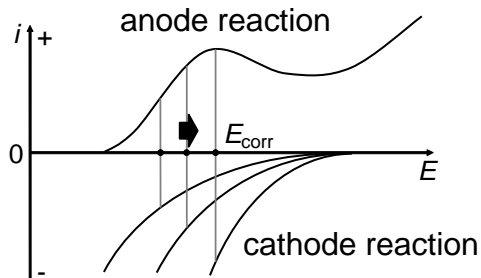


Fig. Schematic diagram of the polarization curves

Cathode currents increase with the increase of oxidant CuCl_2 concentration.



The electrode potential shifts to noble direction.

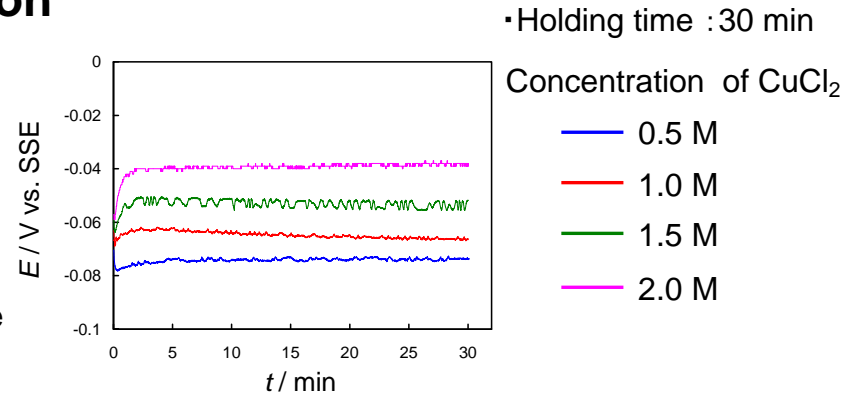
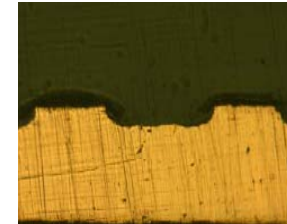
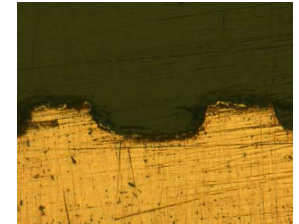


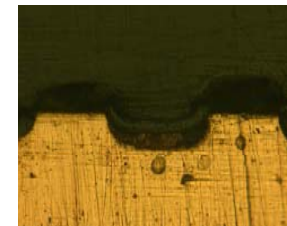
Fig. Potential-time curves
 (in CuCl_2 + 0.2 M HCl + 1.0 M NH_4Cl)



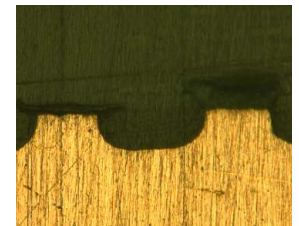
(a) 0.5 M CuCl_2



(b) 1.0 M CuCl_2



(c) 1.5 M CuCl_2



(d) 2.0 M CuCl_2

Fig. The cross-section of the electrode

● Conclusions

- The mechanism of etching for Cu wire was explained by mixed potential theory.
- The dissolution shapes provided by controlling electrode potential were same as those by etching with oxidant.
- The potential dependence of the etching pattern was explained by the dissolution mechanism of Cu.