

## **A New Copper Etching Process by Using Electrically Mediation For PWB Manufacturing Application**

J.J. Sun<sup>1</sup>, E.J. Taylor<sup>1</sup>, L.E. Gebhart<sup>1</sup> and Alan West<sup>2</sup>

1. Faraday Technology, Inc. 2. Columbia University

### **ABSTRACT**

This paper describes the development of an improved printed circuit board etching manufacturing process, which will allow finer features to be produced on the board and allow for higher density packaging to accommodate flip-chip carriers, chip scale packages, and ball grid array technology. In contrast to traditional spray etching, which relies on strong chemical etchants and convective forces to remove material, the process described is based on electrical mediation of the etching process. The proposed process will allow etching of lines and spaces to below 10  $\mu\text{m}$  in width and will etch anisotropically. Initial results will be discussed.

For more information, contact:

Phillip Miller  
Faraday Technology, Inc.  
315 Huls Drive  
Clayton, OH 45315

Phone: (937)-836-7749  
FAX: (937)-836-9498

## Introduction

As electronic devices become smaller and more functionally integrated, the design of interconnect printed wiring boards (PWB) is moving in the direction of finer pitch surface tracks, smaller diameter through holes and vias, and thicker boards to provide higher circuit densities. The leading method currently used to produce a PWB is the subtractive method, usually spray etching, to achieve the desired surface pattern.<sup>i</sup> This technique relies on chemical etchants, which most are alkaline ammonia, hydrogen peroxide-sulfuric acid, and cupric chloride to dissolve the unnecessary parts of the copper layer to form a circuit. However, spray etching does not perform well due to mass transport limitations of the chemicals for the smaller spaces, typically for line widths less than 75  $\mu\text{m}$ .

With spray etching, it is the hydrodynamic factors that limit the possible conductor width and spaces. In large features, the etchant can penetrate into the feature and good etching is easily achieved. When the feature sizes drop below 75  $\mu\text{m}$ , the diffusion layer cannot penetrate the features, and the process becomes mass-transport limited. The etching rate slows considerably and the etch process becomes diffusion controlled. The copper etches isotropically, which leads to considerable undercutting of the resist and the conductor walls have a typical slope and footprint at the bottom<sup>ii</sup>. This results in necking of the copper lines, and affects the resistance and impedance of the PWB, the line spacing, and ultimately the size of the board.

With spray etching, aggressive acidic or alkaline etchants are used to dissolve copper. As the copper concentration in the etchant increases, the performance of the etchant degrades. Therefore, additives must be included in the etchant to bind the copper, and the etchant must be either continually regenerated or dumped to waste treatment. In addition, the choice of chemical etchant is often a compromise between etch rate, capacity and compatibility with photoresist. For example, acidic cupric chloride has a faster etch rate than alkaline ammonium chloride solution, but is incompatible with tin solder.<sup>i</sup>

For chemically mediated etching processes, spray etching is preferred over immersion etching, for higher etch rates. Horizontal spray etching is preferred over vertical etching, for better definition of lines and spaces. However, puddling of etchant in the middle of the board, and on the top of the board, causes nonuniformity in the degree of etching across the board.<sup>iii</sup>

Currently, a new technology is under development, which uses DC (direct current) etching to control copper dissolution.<sup>iv</sup> A DC field is applied between a cathode and the panel. The cathode is placed a few millimeters up to several centimeters from the panel to improve the primary current distribution. A strong chemical etchant is used, to combine both electrochemical and chemical etching of the copper foil. Some promise has been shown by this technology in improving the Etch Factor to between 3 and 10 for lines and spaces 20 to 100  $\mu\text{m}$  in width using 9

to 17  $\mu\text{m}$  thick copper foil and 20 to 35  $\mu\text{m}$  thick photoresist. For lines and spaces as low as 10  $\mu\text{m}$  in width, using 5  $\mu\text{m}$  thick copper foil and 2  $\mu\text{m}$  thick photoresist, the estimated Etch Factor was 4. Typical copper foil and photoresist thickness are on the order of 30-35  $\mu\text{m}$ , so the etch depth in these experiments are not so high as those used in production.

In attempts to obtain an acceptable and effective etching process to address these limitations, the electrically mediated etching process has been evaluated in feasibility studies for fine pitch applications. The process can easily focus or defocus the current distribution by using electrical mediation parameters and obtain anisotropic etching of lines and spaces on PWBs by control of etchant mass transport into and out of the features. The major advantages of using electrochemical etching techniques as compared to chemical etching are: 1) use of nonaggressive electrolytes, 2) higher metal removal rates, and 3) better wall slope control (anisotropy), and 4) low cost.<sup>v</sup>

### Faradaic Etching Process

The electrically mediated etching process is based upon the use of a charge modulated waveform (shown in Figure 1), which consists of an anodic pulse current density,  $i_a$ , an anodic on time,  $t_a$ , and an off-time,  $t_0$ . A cathodic pulse current density,  $i_c$ , and a cathodic on time,  $t_c$ , may also be required for enhanced process control. The sum of the anodic and cathodic on-times and the off-time is the period,  $T$ , of the modulation and the inverse of the period is the frequency,  $f$ , of the modulation. The anodic,  $\gamma_a$ , and cathodic,  $\gamma_c$ , duty cycles are the ratios of the respective on-times to the charge modulated period. The average current density or net etching rate is given by:

$$\text{Etching rate} = i_a \gamma_a - i_c \gamma_c \quad (1)$$

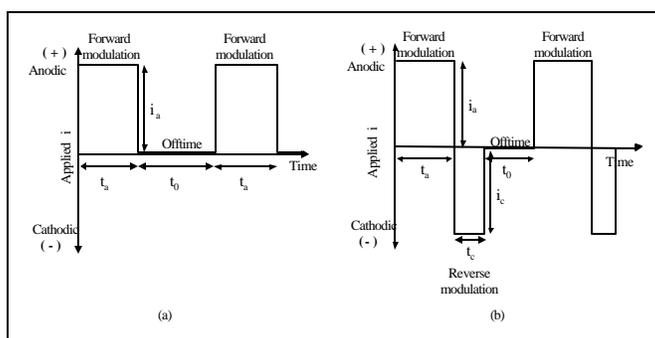
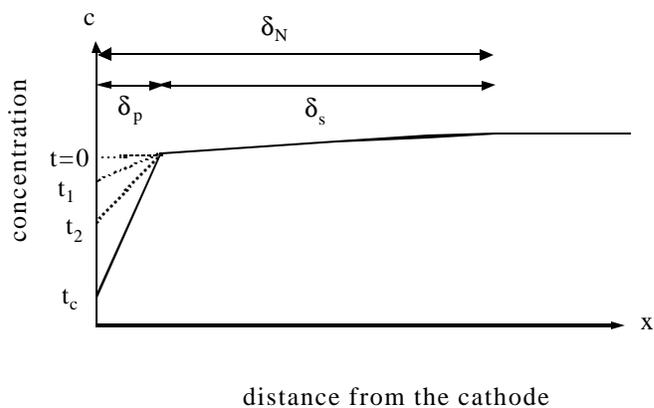


Figure 1: Diagram of generic faradaic waveforms.

During charge modulated waveform controlled electrolysis, a “duplex diffusion layer” develops. As shown in Figure 2, the duplex diffusion layer consists of a stationary layer and an inner pulsating layer. By assuming a linear concentration gradients across the pulsating diffusion layer and conducting a mass balance,  $Ib^{vi,vii}$  derived the following relationship between the pulsating diffusion layer thickness ( $\delta_p$ ) and the on-time of the pulse as:



- $\delta_p$  : thickness of the pulsating diffusion layer
- $\delta_s$  : thickness of the stationary diffusion layer
- $\delta_N$  : thickness of the diffusion layer under DC control

Figure 2. Schematic representation of the duplex diffusion layer

$$\delta_p = 2((Dt_{on})/\pi)^{1/2} \quad (2)$$

where “D” is the diffusion constant, “ $t_{on}$ ” is the on-time of the pulse and “ $\delta_p$ ” is the pulsating diffusion layer. Since the pulsating diffusion layer is determined by the on-time of the pulse, we refer to it as the “electrodynamic diffusion layer.” As shown in Figure 3, proper selection of the electrodynamic diffusion layer can convert a macroprofile to a

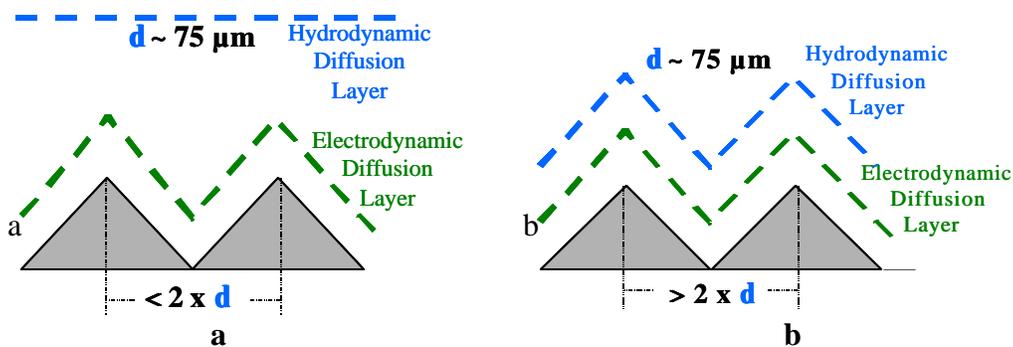


Figure 3. Relationship between the hydrodynamic diffusion layer and the electrodynamic diffusion layer for (a) microprofile (b) macroprofile.

smaller macroprofile or convert a microprofile to a smaller microprofile. In a microprofile (Figure 3a), the roughness of the surface is small compared with the thickness of the diffusion layer and the current distribution is non-uniform. In a macroprofile (Figure 3b), the roughness of the surface is large compared with the thickness of the diffusion layer, and the diffusion layer tends to follow the surface contour. Consequently, under mass transport or tertiary control, a macroprofile yields a uniform current distribution and conformal dissolution during etching.

For example, when the etching line (space between resist patterns) is about  $100\ \mu\text{m}$  or less, the opening is less than two times the thickness of the diffusion layer (assuming  $50\ \mu\text{m}$ ). Consequently, as depicted in Figure 4a, these features are hydrodynamically inaccessible, *i.e.*, the diffusion layer cannot follow the contour of the feature. Consequently, these cases represent a microprofile. The optimum etching process should yield metal dissolution from the center and conformally along the space shape, not from the sidewalls. Therefore, the anodic modulation should convert the microprofile to a macroprofile (Figure 4b) and control the degree of tertiary current distribution to accomplish this goal. The optimum etching process parameters for microscale features may consist of a relatively short anodic on-time with a high peak anodic current.

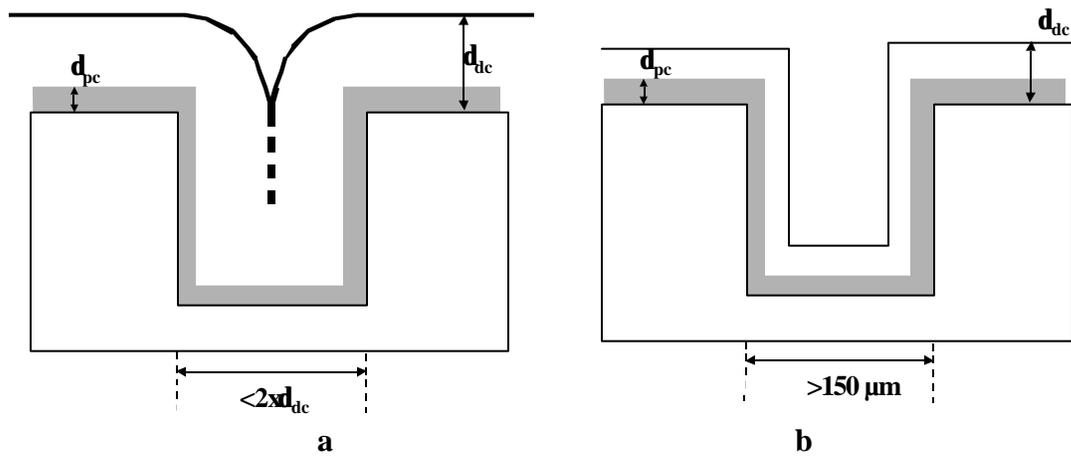


Figure 4. a) Schematic representation of hydrodynamically inaccessible features; b) schematic representation of a macroscale feature.

## Experimental

The experimental investigation of the electrically mediated etching process has been performed on uniformity multipitch test samples. The uniformity multipitch pattern consists of 352 one-in<sup>2</sup> modules, arranged in 22 columns and 16 rows over the 18-in x 24-in panel surface. Figure 5 shows a) the arrangement of four-modules of the uniformity multipitch pattern and b) the pattern design for conductors in each module. The conductor's pattern design is 2-5 mils (conductor width are 2 mils, 3 mils, 4 mils, and 5 mils).

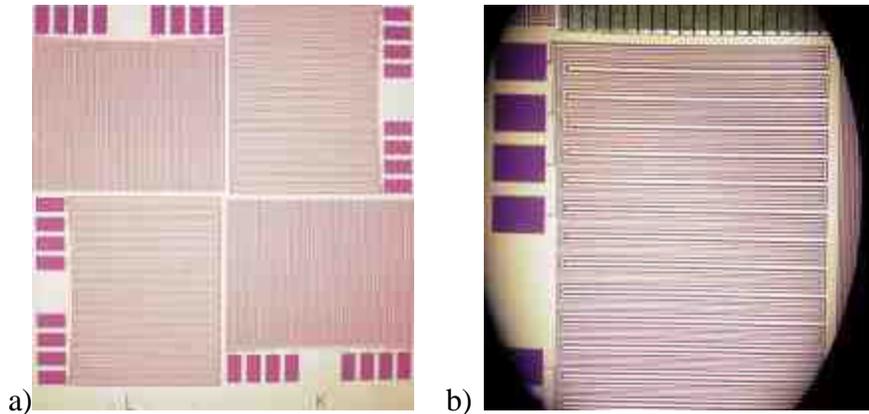


Figure 5. a) Four-module layout of uniformity multipitch pattern b) 2- to 5-mil conductor pattern design

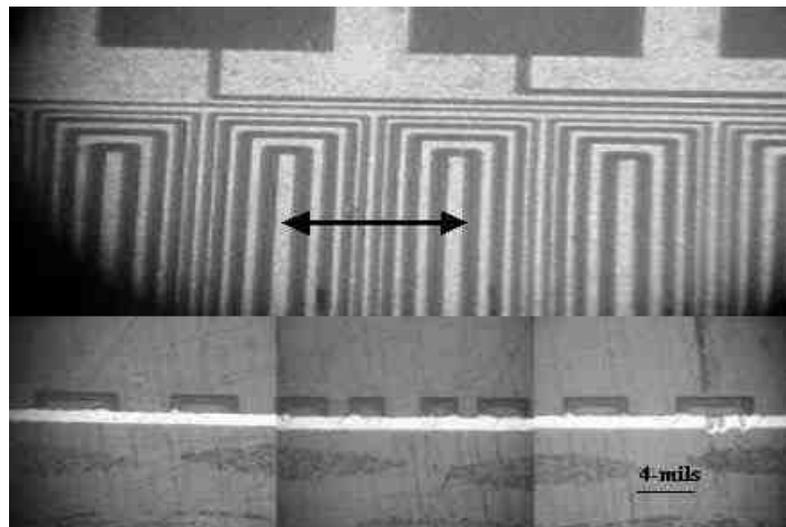


Figure 6. Conductor line design (above) and cross-section of lines and spaces (L/S) pattern

As shown in Figure 6, conductor lines design in each module and the test sample cross-section, with additional consideration of Etch Factor (~4) and Undercut for spray etching process, the width of lines and spaces (L/S) vary in each module from about 140/140  $\mu\text{m}$  (~5.5/5.5-mils), 140/90  $\mu\text{m}$  (~5.5/3.5-mils), 115/65  $\mu\text{m}$  (~4.5/2.5-mils), 90/40  $\mu\text{m}$  (~3.5/1.5-mils), 65/65  $\mu\text{m}$  (~2.5/2.5-mils), 65/40  $\mu\text{m}$  (~2.5/1.5-mils), 90/65  $\mu\text{m}$  (~3.5/2.5-mils), and 115/90  $\mu\text{m}$  (~4.5/3.5-mils) in compensation for line-width reduction during the chemical etching process. The thickness of dry film resist is 35  $\mu\text{m}$  (1.4-mil) and copper foil is about 25  $\mu\text{m}$  (1-mil).

Table I. Test Matrix

Test No.	$\gamma_a$ (%)	F (Hz)	$T_{\text{on}}$ (ms)	$T_{\text{off}}$ (ms)	$V_{\text{ave}}$ (V)	$V_{\text{peak}}$ (V)
1	100	DC	50 sec	0	5	5
2	20	833	0.24	0.96	3	15
3	20	108	1.90	7.3	3	15
4	20	108	1.90	7.3	5	25
5	20	833	0.24	0.96	5	25
6	80	833	7.30	1.9	3	6.25
7	80	833	0.96	0.24	5	6.25
8	80	108	0.96	0.24	3	3.75
9	80	108	7.30	1.9	5	3.75
10	26	135	1.90	5.5	5	19.2
11	62	135	4.6	2.8	5	8
12	62	135	4.6	2.8	5	9

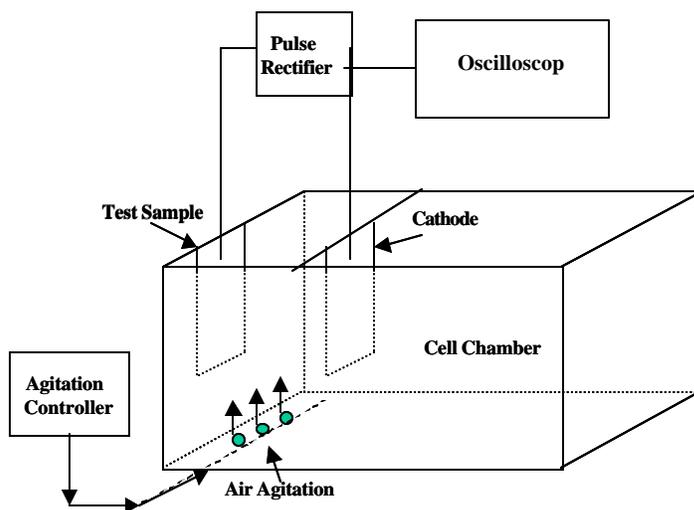


Figure 7. Schematic of the experimental apparatus

The initial experiments for evaluation of the electrically mediated etching process were conducted in the Hull-cell system using different electrolytes and electric mediation waveform parameters. The test matrix for electrical mediated waveform parameters comparison was designed using a full factorial method by MINITAB software based on numerical simulation results,<sup>viii</sup> as listed in Table I. The experimental apparatus illustrated in Figure 7 includes a cell chamber that holds 275 ml electrolyte, an air agitation controller, a cathode holder, a pulse rectifier and an oscilloscope that was used to verify the modulated waveform output from the pulse rectifier. The size of test samples was 2-in x 1-in, which was cut from the 18-in x 24-in panel, with a 1-in<sup>2</sup> module of exposed etching test area. Neutral salts such NaNO<sub>3</sub> and a mixture of NaNO<sub>3</sub> + NaCl were used as electrolytes. The air agitation was controlled at ¼ low level during most of the test period. The etching process was controlled by voltage under an average of 3 and 5 volts. The all experiments were conducted at room temperature and the test duration was 50 sec to match the duration in a manufacturing process.

During etching, as the depth of etch proceeds vertically, the sidewalls tend to etch side ways and produce an undercut action. The degree to which this occurs is known as the *etch factor*, defined as the ratio of depth to side attack (see Fig. 8). Since *undercut* is included in the minimum conductor width measurement, *etch factor* (measurement of the degree of undercut) present is not usually required. The K-value is a constant that represents the ratio of the vertical etching rate to horizontal (side) etching rate to measure the etched copper foil dimension in the space. When the K-value is large (>1), the copper-etching rate along the vertical direction is relatively higher than the side etch rate in the space. This condition is advantageous for forming a fine pattern. In this paper, the etch quality is defined by measuring the conductor (copper) width at the top and bottom together with the minimal conductor width within the top and bottom. The undercut, etch factor, and K-value are also calculated to compare with the target width that would be expected from a chemical etching process

Subsequently, each test sample was cross-sectioned and mounted to evaluate the etching quality by using a microscope. Based on the parameters generally used for chemical etching evaluation, the copper vertical etch distance (copper foil thickness – the remaining copper thickness at the deepest part in the space) and the horizontal etched distance (side etch) in photographs were measured to analyze the test results for the etching process. Some etching evaluation parameters, such as undercut, K-value and etch factor, were calculated to compare the etching quality of the etching process with the chemical etching process illustrated in Figure 8.

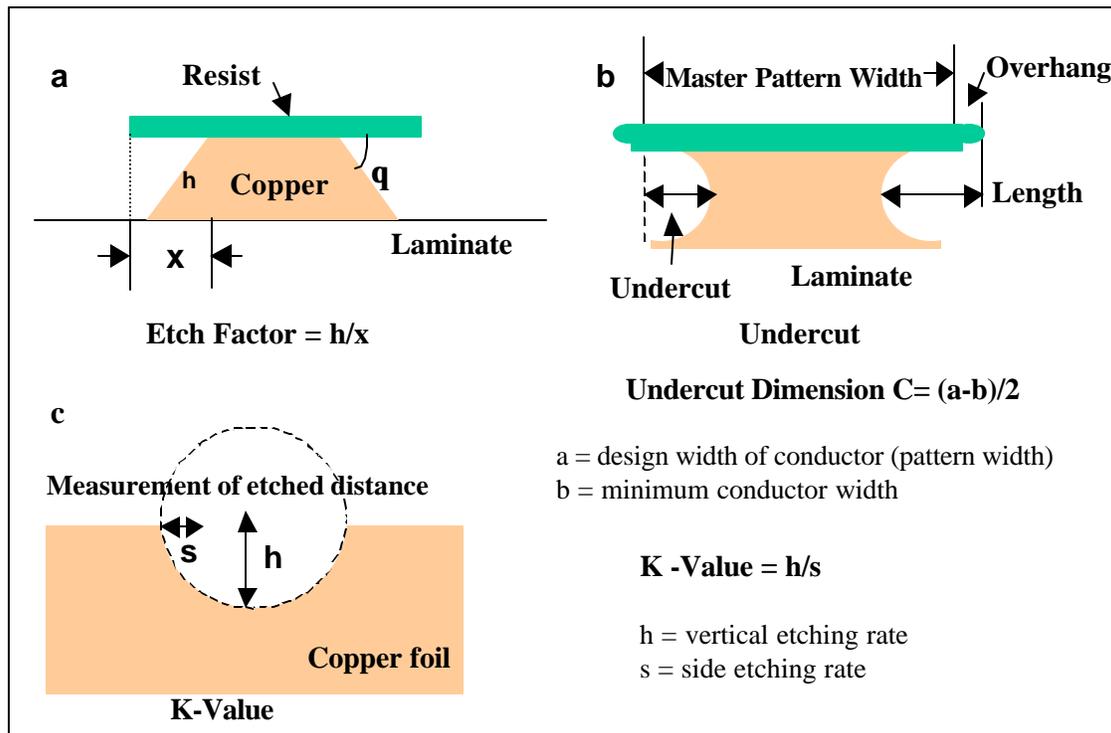


Figure 8. Etched data measurements

## Results and Discussion

The target performance criterion for the initial experimental study was to evaluate if it is possible to obtain an anisotropic etching process by controlling the electrical mediation parameters in place of chemical mediation. The data listed in Tables 2 and 3 show the experimental results of etching the smallest and largest pitch on the samples using different electrically mediated waveform parameters and electrolytes. The test data were measured from the photos of samples' cross-section, as shown in Figure 9. The etching rate on vertical and side directions was given by:

$$\text{Etch rate } (\mu\text{m}/\text{min}) = s \text{ (or } h) \times 25 \times 60 / \text{etching time (sec)} \quad (3)$$

The target etch factor and undercut data expected from the current chemical etching process are  $\theta = 4$  and  $C=0.25$  mils on each side, which are designed in the patterns. The conductor width and space width should be within  $L=5.5\text{-}5\text{-mils}/S=5.5\text{-}6\text{-mils}$  ( $138\text{-}125/138\text{-}150 \mu\text{m}$ ) for the largest pitch dimension and  $L=2.5\text{-}2/S=1.5\text{-}2\text{-mils}$  ( $62\text{-}50/38\text{-}50 \mu\text{m}$ ) for the smallest pitch dimension. The K-value in chemical etching process is around 2.5 to 3. All test results were compared with the target data.

Table 2. Test Data for L/S = 5.5/5.5 (Target L/S = 5/6 mils-125/150 μm)

Test No.	Test Conditions (ms) or (V)			Copper Width (mils)			Copper removal from space (mil)		Under-cut (mil)	K value	Etch Factor (q)
	T <sub>on</sub>	T <sub>off</sub>	V <sub>p</sub>	Top	Bott.	b	Side	depth			
1	DC	0	5	3.67	3.67	3.67	1.19	1.0	0.92	0.84	>>10
2	0.24	0.96	15.0	4.88	6.07	4.88	0.32	0.9	0.31	2.81	1.68
3	1.90	7.30	15.0	4.63	4.63	4.63	0.91	1.0	0.43	1.09	>>10
4	1.90	7.30	25.0	3.57	3.57	3.57	1.15	1.0	0.97	0.87	>>10
5	0.24	0.96	25.0	5.03	6.04	5.03	0.27	1.0	0.23	3.7	1.98
6	7.30	1.90	6.25	3.59	3.59	3.59	0.92	1.0	0.96	1.09	>>10
7	0.96	0.24	6.25	4.78	5.9	4.78	0.24	0.6	0.36	2.5	1.78
8	0.96	0.24	3.75	5.50	6.01	5.5	0	0.4	0	>>10	3.92
9	7.30	1.90	3.75	4.41	5.75	4.41	0.41	1.0	0.54	2.4	1.49
10	1.90	5.50	19.0	5.02	5.80	5.02	0.24	0.75	0.24	4.1	2.55
11	4.60	2.80	8.0	4.72	5.56	4.72	0.36	1.0	0.39	2.79	4.08
12	4.60	2.80	9.0	5.46	5.46	5.46	0.02	1.0	0.02	50	>>10

Note: b is minimal conductor width

Table 3. Test Data for L/S = 2.5/1.5 (Target L/S = 2/2 mils-50/50 μm)

Test No.	Test Conditions (ms) or (V)			Copper Width (mils)			Copper removal from space (mil)		Under-cut (mil)	K value	Etch Factor (q)
	T <sub>on</sub>	T <sub>off</sub>	V <sub>p</sub>	Top	Bott.	b	side	depth			
1	DC	0	5	1.01	1.00	1.00	0.71	1.0	0.75	1.4	>>10
2	0.24	0.96	15.0	1.79	2.86	1.79	0.47	1.0	0.35	2.13	1.87
3	1.90	7.30	15.0	1.21	1.21	1.21	0.60	1.0	0.64	1.67	>>10
4	1.90	7.30	25.0	0.53	0.53	0.53	0.98	1.0	0.99	1.01	>>10
5	0.24	0.96	25.0	1.88	2.62	1.88	0.31	1.0	0.31	3.2	2.70
6	7.30	1.90	6.25	0.66	0.66	0.66	0.89	1.0	0.92	1.12	>>10
7	0.96	0.24	6.25	1.75	3.75	1.75	0.28	0.61	0.37	2.17	1.0
8	0.96	0.24	3.75	2.62	3.44	2.62	0	0.54	0	>>10	2.4
9	7.30	1.90	3.75	1.52	3.25	1.52	0.42	1.0	0.49	2.4	1.16
10	1.90	5.50	19.0	1.67	3.89	1.67	0.39	1.0	0.41	2.57	0.90
11	4.60	2.80	8.0	1.60	2.10	1.60	0.5	1.0	0.25	2.0	4
12	4.60	2.80	9.0	2.30	2.50	2.30	0.13	1.0	0.10	7.6	10

Note: b is minimal conductor width

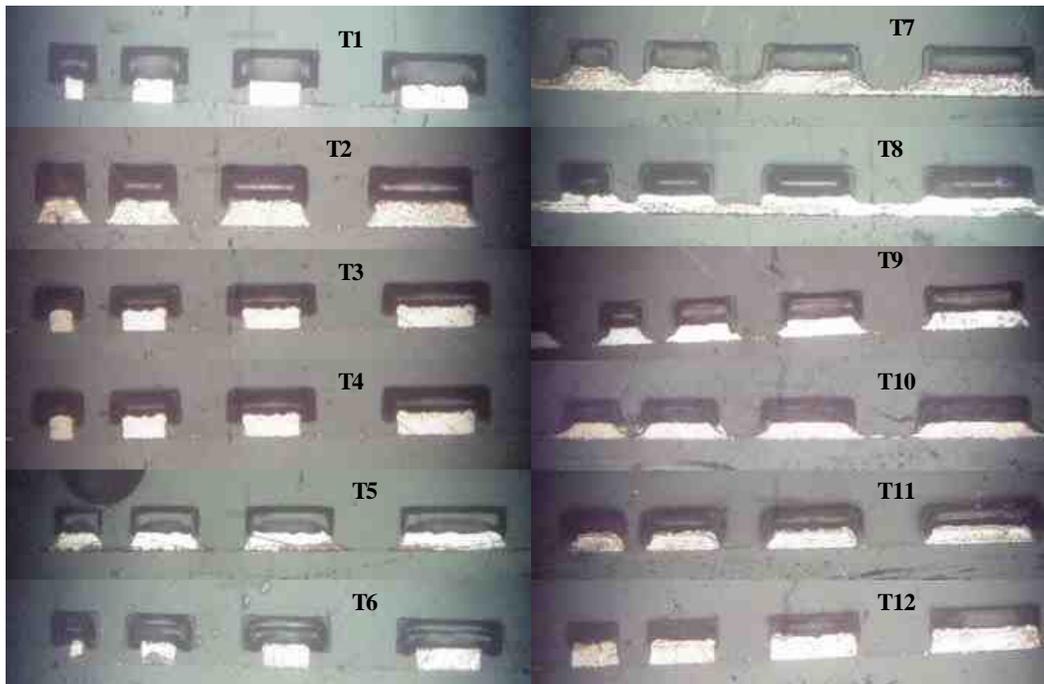


Figure 9. Photo picture of test samples cross-section

In Figure 10 the test results indicated that the etch target can be reached by using the electrically mediated etching process. Compared to the chemical mediated etching process, a higher K-value and lower undercut value (very slow side etching rate) can be obtained using the electrically mediated etching process for different sizes of lines and spaces (see Fig.9-T12) using appropriate electrically mediated process parameters, such as electrolyte, flow conditions, and electrically mediated waveform. In addition, the etching process can also provide a straight sidewall of space to achieve a high etch factor ( $\gg 10$ ) due to the conformal current distribution following the space.

Based on the results of numerical simulation, the anodic peak voltage and anodic modulated on-time are important factors of the electrically mediated etching process. The effect of these electrically mediated parameters on the copper etching rate in 40  $\mu\text{m}$  and 125  $\mu\text{m}$  spaces is presented in Figures 11 to 13. The copper etching rate in the vertical direction is proportional to the peak voltage up to 10 volts regardless of the space size (see Fig.11). A small size of space (40  $\mu\text{m}$ ) has a low side etching rate compared to a large size space with increasing voltage ( $>6.25$ ). These conditions are advantageous for controlling the etching process when etching finer lines due to less undercut attack on a small space to avoid the over etching of fine conductor lines.

As shown in Figure 12, the side etching rates are lower in both large and small size of spaces when the anodic on-time is around 1 ms. However, the vertical etching rate in large spaces is inconsistent with the rate in small spaces that can cause etching process failure due to the copper being incompletely removed. High vertical etching rate with a relatively low side etching rate can

be obtained for both large and small line spaces by controlling the anodic on-time around 4 to 5 ms. In addition, the effect of modulated frequency on the vertical and side etching rate (see Fig.13) should be considered because the anodic on-time is determined by the modulation period (frequency). High frequency tends to increase the side etching rate and reduce the vertical etching rate. The higher K-value ( $K=7.5/K=50$  for 1.5/5.5 mil space) can be achieved by controlling the modulation frequency around 135 Hz.

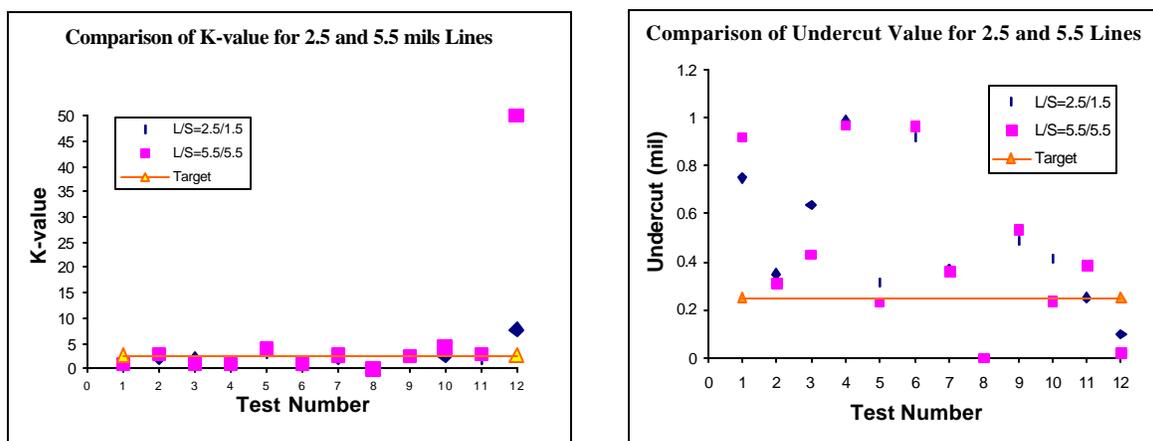


Figure 10. Comparison of electrically mediated etching test results with target data

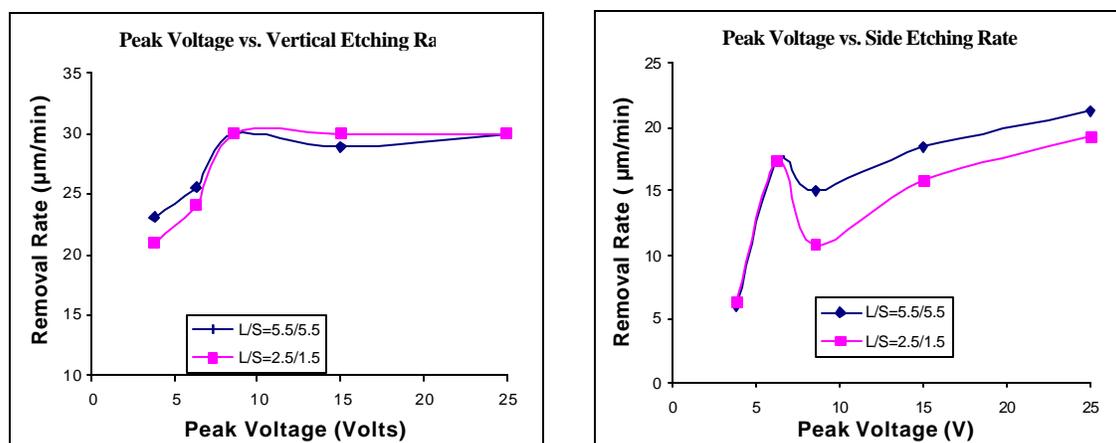


Figure 11. The effect of peak voltage on copper removal rate

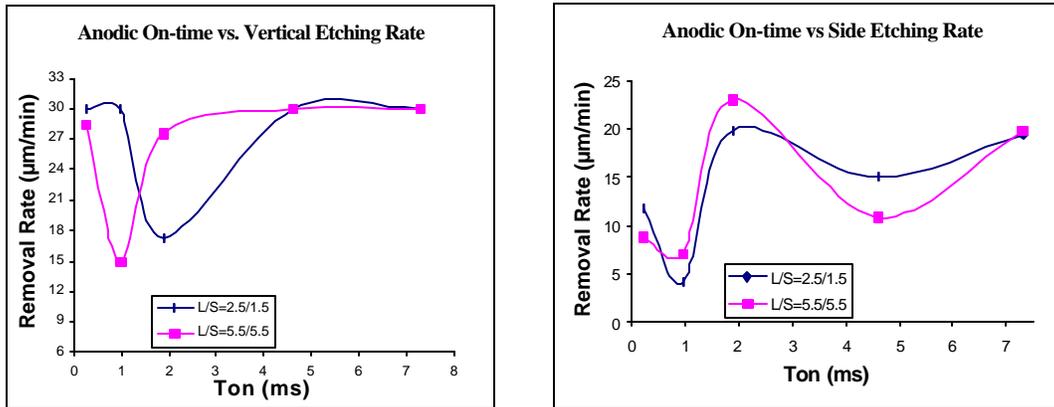


Figure 12. The effect of anodic on-time on copper removal rate

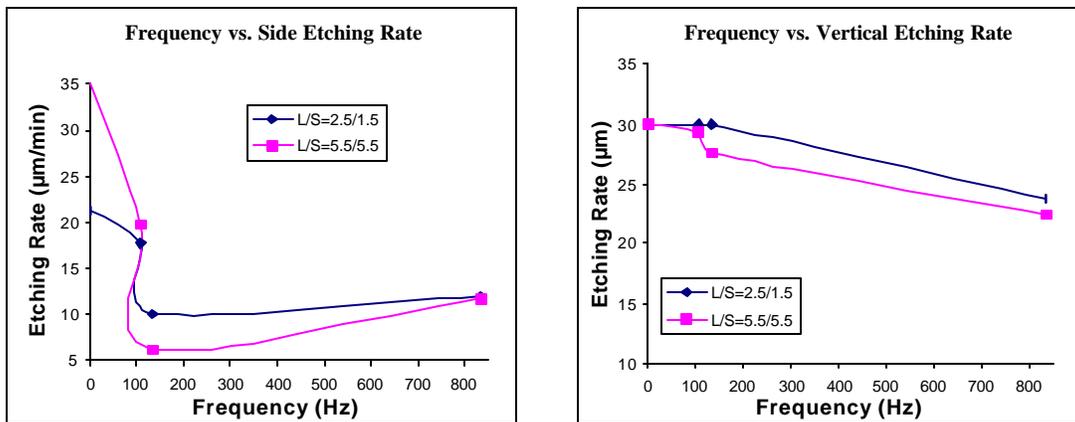


Figure 13. The effect of frequency on copper etching rate

## Summary

The lab-scale experimental study shows the possibility of etching different sizes of lines and spaces using the electrically mediated etching process. The theoretical benefits of the process presented in this paper have also been demonstrated during the feasibility study. The process has a comparable etching rate; high etching quality; and an easily controlled neutral bath compared to the chemical etching process. The major findings from the initial experimental studies of the electrically mediated etching process are:

- The electrically mediation parameters have an important influence upon the etching rate on the vertical and side direction of the space which determines the etching quality (such as etch factor, undercut, and K-value) during the etching period, especially concerning time and applied voltage.
- Compared to DC etching and chemical etching processes, the electrically mediated Etching process can improve the etching quality parameters such as K=50 (compared to

K=3 for chemical etching) by using appropriate electrically mediated parameters to overcome the mass transport limitations encountered with chemical etching and DC etching.

- The preferred electrically mediation parameters for the etching process in the lab-scale cell are a modulation frequency of ~135 Hz, 60% anodic duty and 6-10 volts of peak voltage.

In addition, by understanding the influence of the electrodynamic diffusion layer on the etching features size, the parameters of the electrically mediated waveforms, such as anodic on-time, peak voltage (or peak current), have to be selected with the best cell configurations and bath chemicals to achieve a high etching rate and etching quality process.

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