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NCMS PWB Program Report Surface Finishes Team Task WBS #3.1.1

Phase I Etching Studies: Chemical Etching of Copper for Improved Solderability

J. O. Stevenson, T. R. Guilinger, F. M. Hosking, F. G. Yost, N. R. Sorensen

Prepared by
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Surface Finishes Team Task WBS #3.1.1**

**Phase I Etching Studies: Chemical Etching of Copper
for Improved Solderability**

J. O. Stevenson, T. R. Guilinger, F. M. Hosking, F. G. Yost, and N. R. Sorensen
Center for Solder Science and Technology
Sandia National Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

Sandia National Laboratories has established a Cooperative Research and Development Agreement with consortium members of the National Center for Manufacturing Sciences (NCMS) to develop fundamental generic technology in the area of printed wiring board materials and surface finishes. Improved solderability of copper substrates is an important component of the Sandia-NCMS program. We are investigating the effects of surface roughness on the wettability and solderability behavior of several different types of copper board finishes. In this paper, we present roughness and solderability characterizations for a variety of chemically-etched copper substrates. Initial testing on six chemical etches demonstrate that surface roughness can be greatly enhanced through chemical etching. Noticeable improvements in solder wettability were observed to accompany increases in roughness. A number of different algorithms and measures of roughness were used to gain insight into surface morphologies that lead to improved solderability.

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NOMENCLATURE

A-D	Analog-Digital
ASME	American Society Mechanical Engineers
CRADA	Cooperative Research and Development Agreement
DEKTAK	Mechanical (Contact) Profilometer
EDS	Energy Dispersive Spectroscopy
EL	Electroless-plated Copper
EP	Electroplated Copper
HT	Heat-Treated Copper
LVDT	Linear Velocity Directional Transducer
NCMS	National Center for Manufacturing Sciences
OSP	Organic Solderability Preservative
PWB	Printed Wiring Board
RA	Arithmetic Average Roughness
R _P	Path Roughness or Surface Area/Lateral Area
R _Q	Root-Mean-Square (RMS) Roughness
R _T	Maximum Peak-To-Valley Roughness
RMA	Rosin, Mildly Active
RST	Optical (Non-Contact) Profilometer (i.e. Rough Surface Tester)
SEM	Scanning Electron Microscopy
WBS	Work Breakdown Structure
XRD	X-Ray Diffraction

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NCMS PWB Program Report

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ABSTRACT Sandia National Laboratories has established a Cooperative Research and Development Agreement with consortium members of the National Center for Manufacturing Sciences (NCMS) to develop fundamental generic technology in the area of printed wiring board materials and surface finishes. Improved solderability of copper substrates is an important component of the Sandia-NCMS program. We are investigating the effects of surface roughness on the wettability and solderability behavior of several different types of copper board finishes. In this paper, we present roughness and solderability characterizations for a variety of chemically-etched copper substrates. Initial testing on six chemical etches demonstrate that surface roughness can be greatly enhanced through chemical etching. Noticeable improvements in solder wettability were observed to accompany increases in roughness. A number of different algorithms and measures of roughness were used to gain insight into surface morphologies that lead to improved solderability.

INTRODUCTION

Rough surfaces and their implications for wettability have been studied by numerous researchers.^[1-10] These studies established the importance of surface roughness in wetting phenomena. Early work by Wenzel described surface conditions necessary for wetting.^[1] Wenzel developed a relationship showing that increases in roughness produce decreased contact angles between wetting liquid and solid substrate. This early result has been investigated for many years in an effort to fully understand wetting behavior on rough surfaces.

Recent work by Romero & Yost^[9] and Yost *et al.*^[10] have emphasized that an additional driving force exists for wetting on rough or grooved surfaces, namely, flow into open channel capillaries. Liquid solder flows into the open channels by capillary action. Solder flow within these V-shaped grooves is dependent on the orientation and physical dimensions of the grooves. Electroplated and electroless-plated copper inherently possess some degree of open capillary roughness that encourages solder flow. It was our intent to enhance this roughness using various chemical etches. By producing V-shaped grooves through chemical etching, we

would have an opportunity to further study the wetting behavior of rough surfaces and perhaps enhance the manufacturability of solder interconnects for electronic assemblies.

As the number of interconnections and the operating speed of electronic devices have increased, the fundamental limits of existing printed wiring board (PWB) manufacturing technologies are becoming increasingly apparent. PWB technology has been challenged to keep pace with advances in interconnection density and operating speed. The domestic PWB industry also faces serious foreign competition from large, well-financed firms.

Today's commercially available solder alloys and processing technologies were developed during a relatively docile period of U.S. industrial activity in which no serious threat was posed by Pacific rim countries, no environmental constraints were placed on producers or users, and continued electronic miniaturization did not provoke accelerated failures in critical equipment. We are now in an intensely competitive manufacturing era and in order to truly have a world class electronics component assembly capability, there is an overwhelming need to define and measure attributes related to

solderability, to dramatically enhance solderability performance to keep pace with advancing density, quality, and reliability requirements, and to integrate this information back into the overall assembly process.

Four consortium members of the National Center for Manufacturing Sciences: AT&T, Texas Instruments, IBM, and Hamilton Standard have established a Cooperative Research and Development Agreement with Sandia National Laboratories to develop fundamental generic technology in the area of PWB materials and surface finishes. The goal of the NCMS-Sandia program is to develop advanced technology to enable the U.S. PWB industry to maintain its position at the leading edge of this crucial technology. Improved solderability of copper substrates is an important component of the Sandia-NCMS program.

An industry-wide desire for improved solder joint manufacturability and reliability has provided the impetus for our efforts to produce "engineered" rough surfaces. The following targets have been identified as potential impact areas:

- Enhanced solder flow on fine pitch circuits
- Equivalent Sn/Pb solderability with Pb-free solders
- Overcome plated-through-hole "weak knee" problem
- Improved adhesion of other metallic or organic coatings
- Fewer solderability defects

As finer pitches continue to be *de rigueur*, the need to ensure complete coverage of solder pads continues to escalate. Incomplete solder coverage is a problem that grows more serious with decreasing pitch. For example, an unwetted area of size "x" clearly has more serious performance consequences for a fine pitch device area of size "2x" than for a gross pitch device area of size "10x". The "defective" region becomes a much larger percentage of the total solder pad area as pitch decreases. For this reason, less than perfect solder flow can be tolerated on a large pitch device. Such a luxury is not afforded on finer pitch devices. The effort to maximize board real estate by increasing density and going to ever finer pitches will certainly exacerbate the potential for problems.

Traditional soldering has been done with lead-based solders and rosin fluxes. New environment, health and waste minimization issues are forcing replacement of older soldering

technologies in favor of improved modern technologies. Conventional Sn/Pb solders exhibit very good area of spread and low contact angles, but recent efforts to reduce or eliminate Pb have produced solders with low area of spread and alarmingly high contact angles. Wenzel's equations encourage us to view surface roughness as a process variable that can be utilized to improve wettability and solderability by increasing area of spread and decreasing contact angle.

Surface roughness has also been successfully used to improve the plated-through-hole "weak-knee" problem observed in many PWB applications.^[11] The thinning of solder coatings at convex areas (i.e. plated-through-holes) on the PWB often leads to diminished solderability in these locations. During the solder dipping or reflow process, molten solder may not flow around these edges, producing the so-called "weak knee". Solder joints at the weak knee are often very poor and are the source of numerous failures.

Surface roughness has the potential for improving the adhesion of copper with other metallic and organic PWB materials. Large increases in surface area promote simple adhesion by providing increased contact sites. The very nature or morphology of the surface is also important in determining adhesion. The presence of dendritic fingers or filamentous structures can increase adhesion by providing the capability for establishing interlocking layers. Exposing and maintaining fresh nascent surfaces is also important. While increased surface areas are generally desirable for promoting adhesion, high surface areas in copper create corrosion concerns due to water condensation in pores and crevices. Rough copper surfaces may require protection with an organic solderability preservative (OSP) coating^[12].

Fewer solderability defects are also a desirable outcome. Surface roughness has the potential to improve solder flow, thereby increasing coverage of the solder pads. Adhesion may also be improved through surface roughness. Increased coverage and improved adhesion have the potential for strengthening solder joints and decreasing defect occurrence.

Surface roughness can be enhanced in a variety of ways. Electroplating has successfully been used to increase the surface roughness of copper substrates.^[10] Electrochemical etching

also has the potential for increasing surface roughness. Electroplating and electrochemical etching both require potentiostatic control (costly for large scale applications). Power supplies can be used in place of potentiostats but the cost to purchase and maintain the capability is still somewhat high.

To avert costly power requirements, discussions with the NCMS PWB Surface Finishes Team resulted in a decision to pursue basic chemical etching as a route to surface roughness. A thorough literature search showed that numerous chemical etches exist for copper.[11,13-30] Table 1 presents a sampling of chemicals that have been used to etch copper. The referenced applications are myriad and do not necessarily seek increased surface roughness. Applications include manufacture of electronic/semiconductor devices and printed circuit boards, dissimilar materials joining, microjoining, diffusion welding, and ultrasonic welding.

<u>Ammonia Solutions</u>	<u>Nitric Acid Solutions</u>
(NH ₄) ₂ S ₂ O ₈ NH ₄ CuCl ₃ NH ₄ Cl, (NH ₄) ₃ PO ₄ , Cu ⁺ [CuNH ₃]Cl ₂ , NH ₃ , NaClO ₂ [CuNH ₃]SO ₄ , NH ₃ , S ₂ O ₈ [Cu(NH ₃) ₄]SO ₄ , NH ₃ , Cl ⁻	dilute HNO ₃ HNO ₃ , HNO ₂ √ HNO ₃ , Cu(NO ₃) ₂ √ HNO ₃ , H ₂ SO ₄ HNO ₃ , CH ₃ SO ₃ H
<u>Sulfuric Acid Solutions</u>	<u>Chloride Solutions</u>
√ H ₂ SO ₄ , H ₂ O ₂ H ₂ SO ₄ , H ₂ O ₂ , NH ₃ √ Na ₂ SO ₄ , H ₂ SO ₄ , H ₂ O ₂ Na ₂ S ₂ O ₈ H ₂ S ₂ O ₈ , halide S ₂ O ₈ , purine, diazine	FeCl ₃ √ FeCl ₃ , HCl CuCl ₂ √ CuCl ₂ , H ₂ O ₂ , HCl Cl ⁻ plasma etch
<u>Organic Solutions</u>	√ initial test suite
amine radicals with UV acetonitrile, gas oxidant acetonitrile, liquid oxidant	

Table 1. Sampling of chemicals that have been used to etch copper.

It was our desire to select candidate chemical etches that would provide us a range of surface morphologies for evaluation of roughness and wettability. Through surface characterization and solderability tests, we hoped to establish a correlation between morphology and solderability. If chemical etching of copper substrates can indeed enhance surface roughness and thereby improve wettability and

solderability, we would achieve our goal of providing NCMS member companies with information to improve the integrity and reliability of solder joints.

SUBSTRATE & ETCH SELECTION

The NCMS PWB Surface Finishes Team and Sandia National Laboratories' Center for Solder Science and Technology have been characterizing several different chemical etches on a range of copper surfaces. As a result of a literature survey, we selected six etches to evaluate from the list in Table 1, two each from Sulfuric Acid Solutions, Nitric Acid Solutions, and Chloride Solutions. The initial test suite of six etches has been denoted with check marks in Table 1. No etches were chosen from Ammonia Solutions or Organic Solutions for this initial test suite because of environmental safety and health concerns about long-term handling and storage of chemicals in these classes.

Three different types of copper-substrate materials were investigated in this study: heat-treated wrought copper (HT), electroless copper (EL), and electroplated copper (EP). The electroless and electroplated copper substrates were coupons sectioned from actual FR-4 boards and chosen because of their real-world applicability. These two substrates are commonly used in the PWB industry.

Electroless and electroplated copper possess inherent degrees of roughness as a result of their individual deposition techniques. Deposition can be performed from a number of different copper baths with varying chemistries. Since neither of these substrates is especially smooth, we chose to include a polished wrought copper substrate in the study as a baseline roughness gauge. These wrought copper substrates were heat treated to increase grain size to more easily observe any preferential attack by chemical etchants. Selective dissolution of grain boundaries is a well-known phenomenon that is often used in metallography to achieve visualization of grain boundaries.[31]

SUBSTRATE & ETCH PREPARATION

The EL and EP samples were obtained from circuit board panels and consisted of FR-4 material sandwiched between opposing copper layers. In their as-received condition they arrived with an OSP coating (imidazole).

Individual test coupons (1 inch x 1 inch) were cut from these panels for testing. The HT samples were 0.25 inch x 0.25 inch.

The first set of etching tests produced samples used for surface roughness evaluation by mechanical profilometry and optical profilometry. Immediately prior to etching, the EL and EP samples were soaked at room temperature for 5 minutes in 100% ethanol to remove the imidazole coating. They were then rinsed in deionized water before immersion in the etchant bath. All EL and EP samples were hydrophilic as they entered their respective etchant baths. No special preparations were applied to the HT samples before they were etched.

All copper surfaces intended for solderability tests (set two) were cleaned in a standard 10% HCl solution for 3 minutes at room temperature. The samples were then rinsed in deionized water before immersion in the etchant bath. These same samples also underwent scanning electron microscopy (SEM) analysis. Only EL and EP substrates were included in the second set of samples.

The six etching solutions were formulated as shown in Table 2.

H₂SO₄/H₂O₂

Prepare 20 vol% H₂SO₄ stock solution (1 part 95-98% H₂SO₄ and 4 parts H₂O). Add 14 mls H₂O₂ per liter of stock solution.

Na₂SO₄/H₂SO₄/H₂O₂

Use 20 vol% H₂SO₄ stock solution. Add 14 mls H₂O₂ and 253 g Na₂SO₄ per liter of stock solution.

HNO₃/Cu(NO₃)₂

Prepare 50 vol% HNO₃ stock solution (equal parts 69-71% HNO₃ and H₂O). Add 253 g Cu(NO₃)₂ per liter of stock solution.

HNO₃/H₂SO₄

Prepare 2 parts 95-98% H₂SO₄, 2 parts 69-71% HNO₃, and 1 part H₂O solution.

FeCl₃/HCl

Prepare 50 vol% HCl stock solution (equal parts 36-38% HCl and H₂O). Add 253 g FeCl₃ per liter of stock solution.

CuCl₂/H₂O₂/HCl

Use 50 vol% HCl stock solution. Add 14 mls H₂O₂ and 253 g CuCl₂ per liter of stock solution.

Table 2. Chemical composition of etching solutions.

EXPERIMENTAL

The first set of etching experiments produced samples used for surface roughness evaluation by mechanical (contact) profilometry and optical (non-contact) profilometry. It was our intent to gather and analyze surface roughness information with each of these two techniques to determine their individual strengths and weaknesses regarding our particular application.

The second set of etching experiments produced samples used for solder wetting balance and SEM evaluation. The wetting balance would provide us with information regarding the effect of the six chemical etches on wettability and solderability performance. SEM analysis would allow close inspection of resulting surface morphologies, perhaps enabling correlation between morphology and wettability.

Mechanical (Contact) Profilometry

A DEKTAK IIA surface profile measuring system (Sloan Technology) was used for our contact surface profile measurements. The DEKTAK IIA is a microprocessor-based instrument used for making measurements on small vertical features ranging in height from less than 100 angstroms to 655,000 angstroms. The instrument is commonly used for developing cross-sectional plots of non-uniform surfaces such as deposited films and optical elements.

The DEKTAK IIA profiles surfaces by moving the sample beneath a diamond-tipped stylus. Surface variations cause the stylus to be translated vertically. Vertical measurements of the stylus are sensed by an LVDT, digitized using an integrating A-D converter, and stored in the instrument's memory. Stored information is displayed on the console's video screen and may be manipulated to magnify specific areas of the trace. Any display can be printed out to provide a permanent record. Profile data can also be transmitted via the DEKTAK IIA's RS232-C port for storage and further analysis.

We designed, developed, and implemented a data acquisition and analysis software package to interface with the DEKTAK IIA RS232-C port. The surface profile measurements are collected and saved to file using an IBM 386-based computer. These files may then be read and analyzed on the IBM or Macintosh platform using the various roughness algorithms we have

19 Etching Conditions

3 Substrates

		HT	EP	EL
No etch	0 sec	X	X	X
H ₂ SO ₄ /H ₂ O ₂	30 sec	X	X	X
	60	X	X	X
	90	X	X	X
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	30 sec	X	X	X
	60	X	X	X
	90	X	X	X
HNO ₃ /Cu(NO ₃) ₂	30 sec	X	X	X
	60	X	X	X
	90	X	X	X
HNO ₃ /H ₂ SO ₄	30 sec	X	X	X
	60	X	X	X
	90	X	X	X
FeCl ₃ /HCl	30 sec	X	X	X
	60	X	X	X
	90	X	X	X
CuCl ₂ /H ₂ O ₂ /HCl	30 sec	X	X	X
	60	X	X	X
	90	X	X	X

Table 3. Mechanical profilometry etching matrix (57 samples).

coded. ASME 846.1 describes quantitative parameters to characterize surfaces from measured profiles.^[32] Parameters are profile-height (amplitude) sensitive, profile-wavelength sensitive, or sensitive to both amplitude and wavelength.

As shown in Table 3, 57 samples (nineteen etching conditions on three substrates) were prepared for contact profilometry measurements. Etch times were 30, 60, and 90 seconds. Each sample was profiled at least two times. A stylus with a 12.5 μm radius tip was used for all measurements. Scan lengths varied between two and four mm with approximately 90% of the scans performed at two mm.

Optical (Non-Contact) Profilometry

An RST surface profile measuring system (WYKO Corporation) was used for non-contact surface profile measurements. The instrument combines interferometric techniques and digital signal processing algorithms to obtain surface profile measurements. When combined with traditional phase-shifting measurement techniques, the claimed result is an instrument capable of profiling surfaces with root-mean-

square roughness ranging from 1 $\text{\AA}$ to over 20 μm and measurement of steps over 100 μm .

The RST profiles surfaces by using white light as the source in an interferometer and measuring the degree of fringe modulation or coherence. Conventional communication theory techniques are used to demodulate the envelope of the fringe signal. Phase shifting interferometric techniques are then used to extend the resolution of the measurement beyond what is capable using white light vertical-scanning alone.

Surface area, arithmetic average roughness, root-mean-square roughness, and maximum peak-to-valley measurements are typical outputs available with the RST technology. The RST instrument is able to provide a number of different report forms incorporating these various measures of roughness. Topographical views of the surface are also possible. The surface roughness data is also stored in electronic file format for later analysis.

We designed, developed, and implemented a software package to read and analyze the RST data files. These files may be read and analyzed on the IBM or Macintosh platform

7 Etching Conditions		3 Substrates		
		HT	EP	EL
No etch	0 sec	X	X	X
H ₂ SO ₄ /H ₂ O ₂	60 sec	X	X	X
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	60 sec	X	X	X
HNO ₃ /Cu(NO ₃) ₂	60 sec	X	X	X
HNO ₃ /H ₂ SO ₄	60 sec	X	X	X
FeCl ₃ /HCl	60 sec	X	X	X
CuCl ₂ /H ₂ O ₂ /HCl	60 sec	X	X	X

Table 4. Optical profilometry etching matrix (21 samples).

using the various roughness algorithms we have coded. ASME 846.1 describes quantitative parameters to characterize surfaces from measured profiles.[32] Parameters are profile-amplitude sensitive, profile-wavelength sensitive, or sensitive to both amplitude and wavelength.

As shown in Table 4, 21 samples (seven etching conditions on three substrates) were prepared for non-contact profilometry measurements. Etch times were 60 seconds. Each sample was measured once. Measurement size was approximately 200 μ m x 200 μ m.

Wetting Balance

Solder wettability was measured with a commercial wetting balance. This experimental method gives quantitative information on the wetting behavior of solder on a metal substrate under a specific set of conditions. The wetting balance tests were performed with 60Sn-40Pb (wt.%) solder at 245°C. Samples were coated with a rosin, mildly active (RMA) flux and

allowed to dry approximately ten minutes prior to wetting balance testing. The immersion times were ten seconds. The tests used an immersion rate of 20 mm/s and an immersion depth of one mm (approximately 0.04 inches).

As shown in Table 5, 70 samples (seven etching conditions on two substrates with five replicates) were prepared for wetting balance experiments. Etch times were 60 seconds. Each sample was evaluated one time on the wetting balance for a total of 70 individual wetting balance traces.

Scanning Electron Microscopy (SEM)

Since only a portion (1 inch x 0.04 inch) of the 1 inch x 1 inch samples were covered with solder at the conclusion of the wetting balance tests, unsoldered areas of these samples were evaluated by SEM to examine their surface morphology. Fourteen samples from Table 5 (seven etching conditions on two substrates) were inspected using SEM.

7 Etching Conditions		2 Substrates	
		EP	EL
No etch	0 sec	5 X	5 X
H ₂ SO ₄ /H ₂ O ₂	60 sec	5 X	5 X
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	60 sec	5 X	5 X
HNO ₃ /Cu(NO ₃) ₂	60 sec	5 X	5 X
HNO ₃ /H ₂ SO ₄	60 sec	5 X	5 X
FeCl ₃ /HCl	60 sec	5 X	5 X
CuCl ₂ /H ₂ O ₂ /HCl	60 sec	5 X	5 X

Table 5. Wetting balance and SEM etching matrix (70 samples).

Figure 1. Traces acquired by mechanical profilometry on HT copper. (a) Comparison of an unetched surface with a 30 sec FeCl_3/HCl etched surface (b) Comparison of the same unetched surface with a 90 sec FeCl_3/HCl etched surface.

RESULTS & DISCUSSION

Profilometry

In the search for improved solderability of copper substrates, one of our goals was to identify an appropriate method for evaluating the roughness of chemically etched surfaces. To correlate surface roughness with solderability, a reliable and accurate roughness metric is required. Mechanical profilometry and optical profilometry produce surface profiles that contain a great deal of roughness information.

Figure 1 displays mechanical profilometry traces on HT copper. These data illustrate the enormous gains in roughness that can be obtained through chemical etching. Table 6 contains a roughness analysis of the three traces in Figure 1 as well as 17 other HT copper traces. While these 20 profiles are a subset of the full HT copper matrix, they are representative and provide a basis for discussion. Path roughness (R_p), arithmetic average roughness (R_A), and root-mean-square roughness (R_Q) were calculated for each profile. R_p is the ratio of two distances: the deflection of the stylus in the vertical (y) direction and the travel of the stylus in the horizontal (x) direction. Under this definition, a perfectly smooth surface would have an R_p of exactly one ($y=x$ where $y=x$). R_p is closely related to surface area.

Etch Solution/Time (sec) Roughness Measure

		R_p	R_A	R_Q
No etch	0	1.00000	130	151
		1.00000	87	102
		1.00000	73	94
$\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$	30	1.00000	108	160
		1.00000	104	118
		1.00000	128	150
	60	1.00000	195	250
		1.00000	131	169
		1.00000	121	154
FeCl_3/HCl	90	1.00000	425	514
		1.00000	346	428
		1.00024	1201	1591
	30	1.00021	1088	1450
		1.00022	1307	1775
		1.00182	3908	4655
	60	1.00165	3260	3898
		1.00147	3514	4189
		1.00271	4538	5385
	90	1.00377	5110	5986
		1.00302	4185	5206

R_p = Path Roughness ($\mu\text{m}/\mu\text{m}$)
 R_A = Arithmetic Average Roughness ($\text{\AA}$)
 R_Q = RMS Roughness ($\text{\AA}$)

Table 6. Sampling of mechanical profilometry results for HT copper.

As seen in Table 6, the unetched sample was measured three times. The calculated R_p was 1.00000 on each occasion, which is consistent with the smooth surface that would be expected on polished wrought copper. R_A and R_Q values of 97 ± 30 Å and 116 ± 31 Å were also determined. The H_2SO_4/H_2O_2 etched samples (30, 60, and 90 sec) all show R_p of 1.00000. These etching times produce no significant increases in surface area over the unetched sample. R_A and R_Q for H_2SO_4/H_2O_2 30 sec and 60 sec etches also show little difference from the unetched sample. However, the 90 sec etch does show an increase in R_A and R_Q . It would appear that the H_2SO_4/H_2O_2 etch slightly increases roughness on the Å scale (as evidenced by R_A and R_Q), but produces no significant increases in surface area (as evidenced by R_p).

The $FeCl_3/HCl$ etch shows significant increases over the unetched sample in R_p , R_A , and R_Q . As $FeCl_3/HCl$ etching time increases, roughness continues to be enhanced. R_p , R_A , and R_Q all appear to be useful metrics for evaluating chemically etched HT copper. Although we have only discussed two etches (H_2SO_4/H_2O_2 and $FeCl_3/HCl$), Table 7 compiles results for multiple trials of all six etches on HT copper. Mean values and standard deviations are shown for the 60 second etch.

Etch of Interest	R_p	R_A	R_Q
Unetched	1.00000 ± 0.00000	97 ± 30	116 ± 31
H_2SO_4/H_2O_2	1.00000 ± 0.00000	149 ± 40	191 ± 52
$Na_2SO_4/H_2SO_4/H_2O_2$	1.00000 ± 0.00000	278 ± 71	354 ± 90
$HNO_3/Cu(NO_3)_2$	1.00337 ± 0.00088	10272 ± 1946	12824 ± 1922
HNO_3/H_2SO_4	1.00049 ± 0.00013	3718 ± 1082	4848 ± 1438
$FeCl_3/HCl$	1.00165 ± 0.00018	3561 ± 327	4247 ± 382
$CuCl_2/H_2O_2/HCl$	1.00009 ± 0.00004	643 ± 149	867 ± 184

60 Second Etch

R_p = Path Roughness ($\mu m/\mu m$)

R_A = Arithmetic Average Roughness (Å)

R_Q = RMS Roughness (Å)

Table 7. Compiled results for mechanical profilometry on HT copper. Results for 30 and 90 sec etches not shown.

Figure 2. Traces acquired by mechanical profilometry on EP copper. (a) Comparison of an unetched surface with a 30 sec $FeCl_3/HCl$ etched surface. (b) Comparison of the same unetched surface with a 90 sec $FeCl_3/HCl$ etched surface.

An identical analysis was conducted on EP and EL copper. Since the EP and EL results were very similar, we only discuss the EP copper analysis. Figure 2 displays mechanical profilometry traces on EP copper. Table 8 contains a roughness analysis of the three traces in Figure 2 as well as 14 other EP copper traces. While these 17 profiles are a subset of the full EP copper matrix, they are representative and provide a basis for discussion.

Etch Solution/Time (sec)		Roughness Measure		
		Rp	RA	RQ
No etch	0	1.00000	3161	3762
		1.00002	4304	4959
		1.00002	1652	2166
		1.00002	3575	4256
		1.00002	3519	4107
H ₂ SO ₄ /H ₂ O ₂	30	1.00006	2047	2493
		1.00005	1447	1810
		1.00005	2778	3376
		1.00006	2213	2643
		1.00006	3136	3838
FeCl ₃ /HCl	30	1.00006	2670	3107
		1.00022	2506	3074
		1.00028	2616	3036
		1.00044	1791	2239
		1.00054	1988	2478
	90	1.00069	2155	2715
		1.00081	2164	2732

Rp = Path Roughness (μm/μm)

RA = Arithmetic Average Roughness (Å)

RQ = RMS Roughness (Å)

Table 8. Sampling of mechanical profilometry results for EP copper.

As shown in Table 8, the unetched sample was measured five times. The calculated Rp was 1.00002 ± 0.00001. The unetched EP copper surface is not as smooth as the unetched HT copper surface. The electroplating process produces an inherently rougher surface and the underlying laminate layers in the FR-4 substrate contribute to a somewhat rippled surface. RA and RQ values of 3241 ± 981 Å and 3850 ± 1037 Å were also determined.

The H₂SO₄/H₂O₂ etched samples (30, 60, and 90 sec) all show Rp of 1.00005 to 1.00006. Unlike the HT samples, etching times in this range produced small but noticeable increases in surface area over the unetched sample. RA

and RQ, however, show considerable variation from measurement to measurement. This variability makes it difficult to assess the RA and RQ effects of the H₂SO₄/H₂O₂ etch on EP copper.

The FeCl₃/HCl etch once again shows significant increases over the unetched sample in Rp. As etching time is increased, roughness (as evidenced by Rp) continues to increase. RA and RQ still appear inconclusive. The RA and RQ metrics are heavily dependent on peak to valley distances. Sampling variations due to undulations in the underlying circuit board cloud comparisons between RA and RQ in the EP samples. Rp appears to be a useful metric. Although we have only discussed two etches (H₂SO₄/H₂O₂ and FeCl₃/HCl), Table 9 compiles results for multiple trials of all six etches on EP copper. Mean values and standard deviations are shown for the 60 second etch.

Etch of Interest	Rp	RA	RQ
Unetched	1.00002 ±0.00001	3241 ±981	3850 ±1037
H ₂ SO ₄ /H ₂ O ₂	1.00006 ±0.00001	2496 ±400	3010 ±518
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	1.00006 ±0.00001	1814 ±94	2289 ±167
HNO ₃ /Cu(NO ₃) ₂	1.00069 ±0.00019	6815 ±1319	8801 ±1674
HNO ₃ /H ₂ SO ₄	1.00015 ±0.00022	2159 ±476	2672 ±584
FeCl ₃ /HCl	1.00049 ±0.00007	1890 ±139	2359 ±169
CuCl ₂ /H ₂ O ₂ /HCl	1.00001 ±0.00000	1777 ±86	2220 ±161

60 Second Etch

Rp = Path Roughness (μm/μm)

RA = Arithmetic Average Roughness (Å)

RQ = RMS Roughness (Å)

Table 9. Compiled results for mechanical profilometry on EP copper. Results for 30 and 90 sec etches not shown.

Etch of Interest	Electroplated Copper				Electroless Copper			
	R _P	R _A	R _Q	R _T	R _P	R _A	R _Q	R _T
Unetched	1.006314	120	152	1.48	1.017418	316	398	2.92
H ₂ SO ₄ /H ₂ O ₂	1.005707	139	175	1.57	1.017627	282	355	3.13
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	1.007031	135	172	1.48	1.020976	299	378	3.40
HNO ₃ /Cu(NO ₃) ₂	1.030769	359	446	3.61	1.019964	461	604	4.59
HNO ₃ /H ₂ SO ₄	1.001754	92	117	1.57	1.016805	375	528	5.05
FeCl ₃ /HCl	1.062241	479	588	3.63	1.026935	310	394	3.08
CuCl ₂ /H ₂ O ₂ /HCl	1.045913	256	322	2.58	1.084099	397	498	4.11

60 Second Etch

R_P = Surface Area/Lateral Area ($\mu\text{m}^2/\mu\text{m}^2$)

R_A = Arithmetic Average Roughness (nm)

R_Q = RMS Roughness (nm)

R_T = Maximum Peak To Valley (μm)

Table 10. Optical profilometry results.

Table 10 shows the optical profilometry results for EP and EL copper. One result from Table 10 is that the unetched EL copper substrate is rougher than the unetched EP copper substrate. This is an inherent difference caused by the nature of the deposition methods. SEM's of representative test surfaces are shown in Figures 3a-3h.

The unetched, H₂SO₄/H₂O₂ etched, and Na₂SO₄/H₂SO₄/H₂O₂ etched EP copper samples exhibit very similar roughness morphologies as seen in Figure 3a - 3c. The R_P, R_A, R_Q, and R_T metrics are very closely grouped for these three conditions. The same trends were seen with the EL copper substrate. An argument might be made that the Na₂SO₄/H₂SO₄/H₂O₂ etch produces a slight increase in R_P for both EP and EL copper, however, the values are similar for these etches.

The HNO₃/Cu(NO₃)₂ etched EP copper sample shows a significant increase over the unetched sample in all four metrics. Not only is surface area increased, but the peak-to-valley dimension

(as evidenced by R_A, R_Q, and R_T) is increased considerably. An SEM of this substrate is shown in Figure 3d. The HNO₃/Cu(NO₃)₂ etched EL copper shows the same trend with respect to peak-to-valley measurements, but surface area does not appear to be much increased over the unetched sample.

We postulate that the differing morphologies of the EP and EL copper substrates play a role in determining the result of the HNO₃/Cu(NO₃)₂ etch. Perhaps the inherent nature of the EL copper combined with the chemical action of the HNO₃/Cu(NO₃)₂ etch does not promote the roughening required for increased surface area, although it does seem to support the creation/enhancement of large peak-to-valley distances. Based on these results, one would expect to find fairly large peaks and valleys in the etched EL copper, but with somewhat smooth walls. The etched EP copper, however, should possess the same fairly large peaks and valleys, but with an increased degree of roughening along the walls.

Figure 3. SEM's of test surfaces. 60 sec etches and EP copper substrates except as noted. Micrographs a - f at 8000X magnification with 1 μ m fiduciary marks. Micrograph g at 7500X mag with 1 μ m fiduciary mark. Micrograph h at 2000X mag with 10 μ m fiduciary mark. a) Unetched b) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ c) $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ d) $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ e) $\text{HNO}_3/\text{H}_2\text{SO}_4$ f) FeCl_3/HCl g) FeCl_3/HCl (90 sec) h) $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ (EL Cu)

The $\text{HNO}_3/\text{H}_2\text{SO}_4$ etched EP copper sample appears to be smoother than the unetched EP copper substrate. Not only is the surface area of the etched sample much smaller, but the peak-to-valley dimensions are slightly decreased as well. Apparently, the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch effectively smoothes the EP copper surface. The SEM of this substrate, shown in Figure 3e, confirms this observation.

The action of the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch on EL copper is not quite as clear. The surface area appears largely unaffected by the etch, but the peak-to-valley metrics are slightly increased. This behavior seems to be consistent with the $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ etched EL copper, where we postulated that the interaction of the etch with EL copper does not promote the roughening required for increased surface area, although it does seem to support the growth of peak-to-valley distances. Based on these results, one would also expect to find fairly large peaks and valleys in the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etched EL copper, but again, with somewhat smooth walls.

The FeCl_3/HCl etch produced the largest roughness gains observed on the EP copper substrate. R_p , R_A , R_Q , and R_T reflect very large increases in surface area and peak-to-valley distances. Figure 3f illustrates the roughened surface (60 second etch time). The unusual geometric shapes on the etched surface are a processing side effect to be discussed later. The SEM shown in Figure 3g illustrates the enhanced degree of roughness that can be obtained through increased etching time (90 second etch time).

The FeCl_3/HCl etch also produced increased surface area on the EL copper surface, although the effect is not as pronounced. Interestingly, the peak-to-valley metrics are not changed significantly on the EL copper substrate by etching with FeCl_3/HCl . This behavior is just the opposite of the trend we observed with $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ etched EL copper and $\text{HNO}_3/\text{H}_2\text{SO}_4$ etched EL copper. In these two cases, we postulated that the interaction of the etches with EL copper did not promote the roughening required for increased surface area, although it did seem to support the growth of peak-to-valley distances. Clearly, the FeCl_3/HCl etch interacts with the EL copper in a different fashion. These observations suggest that some individual etches do not perform irrespective of substrate, but rather that the etch/substrate pair is important in determining the actual result.

The $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch was the final condition to be evaluated. In many ways it was the most successful in producing the roughness morphology that we believed would enhance wettability/solderability. Considerable gains in roughness were achieved on EP and EL copper substrates with the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch. As shown in Table 10, surface area (as evidenced by R_p) and peak-to-valley height (as evidenced by R_A , R_Q , and R_T) are significantly increased over the unetched state on both EP and EL copper. The SEM in Figure 3h illustrates the roughened surface that was obtained using the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch. This SEM photo, taken on EL instead of EP substrate, clearly shows the presence of grooves on the etched surface. The etch appears to preferentially attack the grain boundaries of the columnar EL copper structure and also roughen the grains on a finer scale. EP samples also possessed this topology. We will discuss this feature later in the paper. To appreciate the size of the grooves, notice that the magnification of Figure 3h is approximately four times smaller than in Figures 3a-3g.

Table 11 presents a compilation of EP copper data from mechanical and optical profilometry, excerpted from Table 9 and Table 10, respectively. Since it was difficult to interpret peak-to-valley metrics from EP and EL substrates, we restrict our discussion to the surface area metric, R_p . We also believe that R_p more accurately captures the wettability behavior of these systems. This decision is supported by research showing that the roughness ratio in Wenzel's equation relates to the mean square slope of a surface rather than any measure of amplitude.^[10] While R_p is not mean square slope, the two metrics convey similar information.

There are two results in Table 11 that appear to be contradictory. The first of these concerns the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch. The mechanical profilometry result of 1.00015 ranks the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch as one of the rougher etches, exceeded only by FeCl_3/HCl and $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$. The optical profilometry result of 1.001754 shows that the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch produces the smoothest surface. The second apparent contradiction concerns the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch. The mechanical profilometry result of 1.00001 ranks the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched sample as the smoothest surface. The optical profilometry result of 1.045913 places the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch at the rougher end of the spectrum,

MECHANICAL		OPTICAL	
	Rp		Rp
CuCl₂/H₂O₂/HCl	1.00001	HNO₃/H₂SO₄	1.001754
Unetched	1.00002	H ₂ SO ₄ /H ₂ O ₂	1.005707
H ₂ SO ₄ /H ₂ O ₂	1.00006	Unetched	1.006314
Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	1.00006	Na ₂ SO ₄ /H ₂ SO ₄ /H ₂ O ₂	1.007031
HNO₃/H₂SO₄	1.00015	HNO ₃ /Cu(NO ₃) ₂	1.030769
FeCl ₃ /HCl	1.00049	CuCl₂/H₂O₂/HCl	1.045913
HNO ₃ /Cu(NO ₃) ₂	1.00069	FeCl ₃ /HCl	1.062241

60 Second Etch

MECHANICAL Rp = Path Roughness (μm/μm)

OPTICAL Rp = Surface Area/Lateral Area

Table 11. Relative roughness rankings for EP copper (mechanical vs. optical profilometry).

exceeded only by FeCl₃/HCl. A resolution of these contradictions can be obtained by further analyzing the particulars of the mechanical profilometry and optical profilometry techniques.

In the case of the HNO₃/H₂SO₄ etched sample, a 12.5 μm radius tip size was used on the mechanical profilometer and the scan length was 2 mm. Figure 4 shows the etched surface at a scale more illustrative than Figure 3e when discussing the mechanical profilometer. Many long crevices and non-homogeneous surface irregularities are present on the surface. Notice that the 10 μm fiducial mark is on the order of the 12.5 μm radius tip size.

Figure 4. SEM's of 60 second HNO₃/H₂SO₄ etched EP copper (500X mag with 10 μm fiducial mark).

These irregularities would be detected by the stylus over a 2 mm scan length and translated as roughness, as they should, but the roughness can be better described as long range and highly variable across the entire surface of the sample. If the crevices are aligned directionally as they appear, scan direction will greatly affect the roughness value.

Since the surface is observed to be very non-uniform, mechanical profilometry measurements should reflect this condition (confirmed by the large standard deviation of 1.00015±.00022 shown in Table 9). In contrast, the optical profilometry measurement was performed on a 200 μm x 200 μm area thus capturing the shorter range roughness. Further comparison of the SEM's in Figures 3a and 3e show that the HNO₃/H₂SO₄ etched substrate is generally smoother than the unetched sample. Trenches and crevices appear to be non-homogeneously superimposed on this smooth surface.

In the case of the CuCl₂/H₂O₂/HCl etch, a 12.5 μm radius tip size was used on the mechanical profilometer and the scan length was 2 mm. Referring to Figure 3h, the 10 μm fiducial mark is on the order of the 12.5 μm radius tip size. The use of the diamond stylus frequently masks the true profile because the tip fails to reach the bottom of the valleys, will bend over peaks, or can alter delicate or soft surfaces. Without a

priori knowledge of the surface to be measured it is difficult to select the proper tip size for evaluating the surface. The 12.5 μm radius tip size will roll over most of the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch features shown in Figure 3h. The channel diameters are considerably less than 12.5 μm . The smaller scale honeycombed features are one to two microns in size and would certainly not be detected by the 12.5 μm radius stylus. The mechanical profilometry measurement does not accurately reflect the small scale roughness of the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched surface. The optical profilometry measurement captures this small scale roughness because its resolution does not depend on a tip size. The non-contact nature of the measurement also protects surfaces from inadvertent damage.

We do not infer that one technique is more correct than another, but rather that each technique has operational limits. The stylus is a key element in a mechanical surface profilometer and size and shape must be carefully considered in certain analyses. The ideal stylus would faithfully reproduce steps and other features precisely as they exist on a surface. Unfortunately, a real stylus is spherical, causing profiles to have rounded, broadened edges.

Solderability

The wetting balance provides information on the wetting process that can be divided into kinetic and equilibrium data. From the tests, one can extract the contact angle and surface tension (equilibrium parameters) as well as the wetting rate and time to 2/3 the maximum wetting force (kinetic parameters). At this stage of the project, we have not yet attempted to extract the fully quantitative measures such as contact angle, surface tension, wetting rate, and time to 2/3 the maximum wetting force from the data. The main intent of this study was to survey and evaluate the surface morphologies resulting from chemical etches and to establish roughness metrics that would enable us to understand the relationship between roughness and wettability. The wettability/solderability tests were meant to assist in identification of promising candidates. After down-selecting from the initial study group, we will revisit the wetting balance in detail. Other tests, more representative of capillary flow, may also be necessary to better measure the effects of etching on wetting over a roughened surface.

Wetting balance experiments with the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$, and $\text{HNO}_3/\text{H}_2\text{SO}_4$ etches demonstrated that no measurable solderability gains were achieved on EP or EL copper with these solutions. This is in agreement with the profilometry results and SEM's discussed previously which showed no significant roughening from the three H_2SO_4 -containing etches. The exception to roughening is the $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ etch, which produced increased R_A , R_Q , and R_T in both EP and EL substrates. In the EP $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ case, R_p was also increased. Apparently, the increased surface area produced by the $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ etch did not translate into increased wettability/solderability. Perhaps the degree of roughness was insufficient to affect solderability. It is also possible that some surface morphologies leading to increased surface area are not conducive to increased solder flow. The major features on the surface of the EP sample etched in $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ shown in Figure 3d are stacked, faceted protrusions with sheer faces. Rod-like fibril shapes are interspersed across the surface. There appears to be no connecting pathways or vias to promote or sustain solder flow. In fact, in many areas the solder flow could actually be impeded by the protrusions.

The surface morphologies of the unetched, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, and $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ etched are nearly indistinguishable (Figures 3a-3c). Very little roughening was introduced with these two etches so we would not expect any major roughness-based improvements in wettability/solderability.

The smooth non-homogeneous surface produced by the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etch (Figure 3e) is not the type of morphology we would expect to produce wettability improvements. With R_p values below their unetched counterparts, both EP and EL $\text{HNO}_3/\text{H}_2\text{SO}_4$ etched substrates held little promise for solderability gains. This prediction was borne out in wetting balance tests. In fact, wettability was poorer on the etched EL surface compared to the unetched condition. An oxide detected by SEM/EDS could have been a contributory factor in the poor performance of the etched EL sample. The strongly oxidizing nature of the $\text{HNO}_3/\text{H}_2\text{SO}_4$ etching bath could be responsible for leaving the oxide signature on the surface.

The very large R_p value of the FeCl_3/HCl etch on EP copper (1.062241 compared to the unetched condition of 1.006314) was a promising indicator of potential wettability improvements. Figure 5 plots wetting balance results for the FeCl_3/HCl etch vs. the unetched condition on EL copper. Qualitatively, they are difficult to distinguish. Inspection of the full data set shows that some of the FeCl_3/HCl etched samples attained a higher wetting force and produced a greater wetting rate than their unetched counterparts, but it is unclear if these differences are significant.

Figure 5. Wetting balance results for the unetched and FeCl_3/HCl etched conditions on EL copper. Three samples are shown for each condition.

The true performance of the FeCl_3/HCl etch was likely underestimated because most of the etched samples were not ideally processed. SEM/EDS analysis detected a small chlorine presence on the surface of the H_2O rinsed FeCl_3/HCl etched samples (Figure 6). As shown in Figure 3f and Figure 7, CuCl (nantokite) crystals, as identified by X-ray diffraction, were scattered on the surface. The presence of these crystals was a side effect of our etching process. While the nantokite crystals did not cover a large portion of the surface, their presence was reflected in the wetting balance results.

Figure 6. SEM/EDS spectra for H_2O rinsed FeCl_3/HCl etched sample.

Figure 7. CuCl (nantokite) crystals, as identified by X-ray diffraction, were scattered on the surface of the FeCl_3/HCl etched sample. a) 500X overhead view with 10 μm fiduciary mark b) 3500X tilted view with 10 μm fiduciary mark

Wetting balance results for the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch were originally very poor. In this instance, SEM/EDS analysis detected a significant chlorine presence on the surface of the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched samples (Figure 8). The entire surface appeared to be coated with crystalline bodies conformal to an underlying channeled topography as shown in Figure 9. Figures 9a and 9b show SEM's of H_2O rinsed $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched surfaces on EL and EP substrates, respectively. In Figure 9c, an enlargement of Figure 9b, the crystalline bodies may be seen in detail. X-ray diffraction again identified the species as nantokite (Figure 10). As all etches were concluded with a deionized H_2O rinse, we theorized that the nantokite presence was a result of the interaction between the copper removed from the surface and the H_2O rinse.

Figure 8. SEM/EDS spectra for H_2O rinsed $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched sample.

Figure 10. X-ray diffraction spectra identifying CuCl (nantokite) crystals completely covering the surface of the $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched sample.

Figure 9. SEM's of H_2O rinsed $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched samples. a) EL substrate - 500X mag with 10 µm fiduciary mark b) EP substrate - 500X mag with 10 µm fiduciary mark c) Enlargement of b - 5000X mag with 1 µm fiduciary mark

If this dragout/quenching were to produce a nantokite layer on the surface, no subsequent amount of H_2O rinsing would remove the layer since nantokite has a very low solubility in H_2O (.0062 g/100 cc). Nantokite is, however, soluble in HCl. Since copper is only very slightly soluble in HCl, we re-ran the $CuCl_2/H_2O_2/HCl$ etch using an HCl rinse in place of the H_2O rinse. We expected that the HCl rinse would not alter the morphology created by the $CuCl_2/H_2O_2/HCl$ etch. As a result of this processing change, we were able to achieve wetting balance results similar to the $FeCl_3/HCl$ etch. However, it is difficult to capture the improvement with the wetting balance alone.

Figures 11a and 11b show optical micrographs of the soldered unetched sample and soldered $CuCl_2/H_2O_2/HCl$ etched sample, respectively. In Figure 11c, an enlargement of Figure 11b, the etched sample exhibited solder branching not seen on the unetched substrate. Solder was aggressively wetting the surface. Dendritic fingers have spread in advance of the bulk. This behavior could be related to the precursor foot

observed by others.[33-35] Figure 12 is an SEM photo (backscatter imaging mode) showing solder flow into the valleys or grooves. The $CuCl_2/H_2O_2/HCl$ solution was the only etch that exhibited this behavior.

Figure 12. SEM (backscatter imaging mode) of soldered $CuCl_2/H_2O_2/HCl$ etched sample showing solder flow into grooves. Solder is on the bottom half of the photo, flowing upwards. Micrograph at 100X magnification with 100 μm fiduciary mark.

11a)

11b)

11c)

Figure 11. Optical micrographs of soldered samples. a) Unetched b) $CuCl_2/H_2O_2/HCl$ etched c) Enlargement of b at solder front

Figure 13. SEM's of EL copper test surfaces at low magnification. a) Unetched - 500X mag with 10 µm fiduciary mark b) $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched - 200X mag with 100 µm fiduciary mark c) Enlargement of b - 1000X mag with 10 µm fiduciary mark

Figure 13 contrasts the surface morphology of the unetched and $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched sample at low magnification. In Figures 13b and 13c, the etched substrate has a matrix of deep, interconnected grooves spanning the surface. The unetched sample in Figure 13a shows the typical nodular morphology of EL copper deposits. Figure 14 contrasts unetched, FeCl_3/HCl etched, and $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched

surfaces at higher magnifications. The FeCl_3/HCl etch produces uniform small scale roughness, but does not produce V-shaped grooves. The $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etch not only produces small scale roughness, but also deep V-shaped grooves ideal for capillary flow of solder. These grooves are probably caused by the preferential attack of the EL copper grain boundaries by the etch. The actual cause is under investigation.

Figure 14. SEM's of EL copper test surfaces at high magnification. All three micrographs at 8000X magnification with 1 µm fiduciary marks. a) Unetched b) $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etched c) FeCl_3/HCl etched

SUMMARY & FUTURE WORK

We produced physically rougher surfaces through chemical etching of electroplated and electroless-plated copper on FR-4 laminate board. Roughnesses were characterized using mechanical profilometry, optical interferometry, and SEM. Noticeable improvements in wettability/solderability were observed through chemical etching of copper substrates. One of these etches ($\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$) produced a grooved topography and demonstrated excellent wetting behavior, perhaps exceeding the FeCl_3/HCl etch patented by Rockwell.

The wetting balance technique has been used for solderability studies for many years and will continue to be used in the NCMS program. However, many solder joints are formed by filling a gap between a PWB and electronic devices through capillary flow of the molten alloy. The typical wetting balance test does not serve well as a solderability measure for this configuration.

We plan to test the FeCl_3/HCl and $\text{CuCl}_2/\text{H}_2\text{O}_2/\text{HCl}$ etchants on device boards in actual configurations to determine their feasibility. Area of spread and contact angle measurements will provide us with additional information to quantify the real-world beneficial aspects of roughness. We will continue to investigate morphologies that lead to improved solderability.

Environmental stressing (e.g. temperature and humidity aging, etc.) needs to be performed to determine the effects of increased roughness on corrosion susceptibility. We also need to investigate surface roughness and wettability as a function of time and solution concentration. Solution concentration is a potentially important variable and significant gains in wettability can be achieved through process optimization. All tests to date have been performed at single concentrations only.

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