Tin Electroplating/Stripping Evaluation

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M. R. McHenry

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AlliedSignal Inc.
Kansas City Division
P. O. Box 419159
Kansas City, Missouri
64141-6159

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TIN ELECTROPLATING/STRIPPING EVALUATION

M. R. McHenry

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Topical Report
M. R. McHenry, Project Leader

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Abstract

An evaluation was conducted to determine possible replacement chemistries for electroplating and stripping of tin-lead. The driver for this project was two-fold. Our first goal dealt with hazardous waste reduction. It was desired to eliminate lead (a heavy metal) from the electroplating process and thiourea (a known carcinogen) from the stripping process. We also sought to reduce the cost of nonconformance (CONC) realized by this process in the form of rough plating, broken paths, poor solderability, and overetching. Three suppliers' tin chemistries were evaluated as replacements for electroplating and stripping of tin-lead. Based on preliminary testing, one chemistry was chosen, evaluated, and approved for production use.

Summary

In an effort to reduce hazardous waste and cost of nonconformance in Printed Circuit Boards Fabrication, an evaluation was undertaken to replace the tin-lead electroplating and stripping chemistries. The goal in waste reduction was to eliminate lead (a heavy metal) from the plating process and thiourea (a known carcinogen) from the stripping process. It was also our goal to reduce rough tin-lead plating, broken paths, poor solderability, and overetching. A literature search was conducted to identify suppliers for the evaluation. Three suppliers were selected and test panels sent to them

for processing. The test panels were then returned to AlliedSignal Inc., Kansas City Division (KCD) for analysis. The tin plating was evaluated for porosity and grain structure, and surface analysis was conducted after stripping to ensure that all tin was removed and the copper was not contaminated. Based on these results, a supplier was chosen and the chemistries brought in-house for testing. Test panels were processed and evaluated for line width definition and solderability. After successfully passing these tests, a chemistry was chosen and approved for production.

Discussion

Scope and Purpose

This project was undertaken in response to Department of Energy initiatives to reduce hazardous waste. The goal was to reduce hazardous waste and CONC (cost of nonconformance) attributed to the Printed Circuit Boards Fabrication Department associated with the tin-lead plating and stripping processes. The tin-lead plating and stripping processes were specifically chosen to eliminate the use of lead (a heavy metal) from the plating process and thiourea (a known carcinogen) from the stripping process. Major accomplishments benefit all programs.

Prior Work

Materials targeted for reduction were identified through Pollution Prevention Opportunity Assessments conducted during 1990-1992.

Activity

Phase I: Evaluation of Supplier Chemistries

Multilayer capability test panels were sent to three suppliers for processing. The suppliers were MacDermid, Enthone, and Electrochemicals. They were asked to tin plate four epoxy glass multilayer panels and strip two of the panels. All four panels were then returned to AlliedSignal Inc., Kansas City Division (KCD) for analysis. One lot of control panels was plated using our current tin-lead chemistry and stripper. Table 1 displays the process sequences used.

The purpose of the tin process is to act as an etch resist protecting the copper during etching (Figure 1). Since the deposit is tin only, it is also important that the tin be

completely stripped prior to hot air solder leveling (HASL). A process sequence is shown in Appendix A.

Two tests were performed to evaluate the capability of the three supplier processes. The tin deposit was analyzed using scanning electron microscopy for porosity and grain structure. The panels which were stripped had surface analysis performed using an X-ray photoelectron spectrometer (XPS) to ensure complete removal of the tin with no residue.

SEM Porosity Evaluation

Figures 2-5 are photomicrographs showing the deposits at X750 and X5000. The samples are MacDermid, Electrochemicals, Enthone, and our control group, respectively.

Based on the SEM data, the panels were ranked as follows:

Best	2	Electrochemicals
	1	MacDermid
Worst	3	Enthone

The Electrochemicals process was equivalent to our process disregarding the grain structure seen in the tin/lead deposit.

X-ray photoelectron spectrometer (XPS) was used to examine the copper surface after tin stripping. Results are displayed in Appendix B. A contaminate/substrate (tin/copper) ratio was calculated and is displayed in Table 2.

Text continued on page 11.

Table 1. Process Sequences

Sequence	Current Process Solderex LPC Enstrip TL106	Electrochemicals Tin Brite III Solder Strip 150	MacDermid ResTIN PC	Enthone XR-248A Enstrip TL7527
1	PC-4 Cleaner	PC-4 Cleaner	PC-4 Cleaner	PC-4 Cleaner
2	Rinse	Rinse	Rinse	Rinse
3	Sodium Persulfate	Sodium Persulfate	Sodium Persulfate	Sodium Persulfate
4	Rinse	Rinse	Rinse	Rinse
5	Sulfuric Acid	Sulfuric Acid	Sulfuric Acid	Sulfuric Acid
6	Acid Copper	Acid Copper	Acid Copper	Acid Copper
7	Rinse	Rinse	Rinse	Rinse
8	Fluoboric Acid	Sulfuric Acid	ResTin PC Tin Plate	XR-248A Tin Plate
9	Tin-Lead	Tin Brite III Tin Plate	Rinse	Rinse
10	Rinse	Rinse

Figure 1. Pattern Plating Process Sequence

a.

b.

c.

d.

Figure 2. MacDermid Samples at X750 (a, b, c) and X5000 (d)

a.

b.

c.

d.

Figure 3. Electrochemicals Samples at X750 (a, b, c) and X5000 (d)

a.

b.

c.

d.

Figure 4. Enthone Samples at X750 (a, b, c) and X5000 (d)

Figure 5. Control Group Samples at X750 (a, b, c) and X5000 (d)

Table 2. Tin/Copper Ratio

Control	Electrochemicals	Enthone	MacDermid
0.05	0.02	0.08	0.38
0.03	0.03	0.14	0.33
0.04	0.02	0.11	0.46
0.05	0.02	0.16	0.36

These results showed that the Electrochemicals process performed as well as our current process with Enthone coming in a close second and MacDermid a distant third.

In both evaluations the Electrochemicals process performed the best. Electrochemicals Tin-Brite III (tin plating bath) and Sol-Strip 150 (tin-lead stripper) were set up in stores for production use.

Phase II: Qualification (TMS) of Electrochemicals Tin Process

A TMS plan was submitted to the PWB Quality Evaluation Team and approved. The TMS was conducted as follows:

Day 0 Eight control panels, 17-24, were processed through the current tin-lead chemistry using the multilayer capability panel.

The current chemistry was dumped and the Electrochemicals Tin Brite III bath makeup completed.

Day 1 Eight panels (1-8) were plated using the Electrochemicals tin process.

Day 2 Eight panels (9-16) were plated using the Electrochemicals tin process.

The test panels were then processed through the following operations:

- Pumice Scrub
- Etch
- Strip Resist
- Strip Tin/Tin-Lead

The following tests were performed:

1. After tin stripping, path widths were measured on panels 3-5 and 11-13 along with the control panels 19-21. Measurements were taken using the multilayer capability line measurement program on the Optical Gaging Products (OGP). This program measures 5-, 10-, 15-, and 25-mil lines (nine places per panel). The raw data is attached in Appendix C and a summary is shown in Table 3. The Cp and CpK were calculated for comparison between the tin and tin-lead processes.

Table 3. Tin Vs Tin-Lead Electroplating Line Width Data

Panel	Nominal	Front Side	Back Side	Avg. Front	Avg. Back	$\bar{X}_{DBar}$	Stdev	Cp	CpK _(LSL)
3	0.005	0.00255	0.00404	0.00248	0.00416				
4	0.005	0.00227	0.00589	0.00233	0.00589				
5	0.005	0.00427	0.00250	0.00374	0.00256	0.00353	0.00138	0.484	0.127
11	0.005	0.00400	0.00181	0.00422	0.00154				
12	0.005	0.00585	0.00222	0.00467	0.00227				
13	0.005	0.00196	0.00450	0.00209	0.00423	0.00317	0.00135	0.494	0.042
19	0.005	0.00455	0.00195	0.00453	0.00194				
20	0.005	0.00224	0.00506	0.00223	0.00504				
21	0.005	0.00225	0.00539	0.00220	0.00537	0.00336	0.00142	0.469	0.085
3	0.010	0.00711	0.00818	0.00732	0.00845				
4	0.010	0.00750	0.01024	0.00733	0.01017				
5	0.010	0.00858	0.00678	0.00836	0.00662	0.00804	0.00125	1.331	0.809
11	0.010	0.00997	0.00929	0.01004	0.00945				
12	0.010	0.00978	0.00891	0.01007	0.00871				
13	0.010	0.00848	0.00903	0.00841	0.00895	0.00927	0.00070	0.957	3.000
19	0.010	0.01022	0.00868	0.01008	0.00874				
20	0.010	0.00831	0.01110	0.00846	0.01078				
21	0.010	0.00879	0.01055	0.00891	0.01031	0.00941	0.00081	2.050	1.808
3	0.015	0.01210	0.01303	0.01202	0.01322				
4	0.015	0.01212	0.01505	0.01202	0.01487				
5	0.015	0.01319	0.01085	0.01319	0.01085	0.01270	0.00138	1.205	0.650
11	0.015	0.01495	0.01406	0.01488	0.01400				
12	0.015	0.01488	0.01326	0.01480	0.01329				
13	0.015	0.01355	0.01384	0.01350	0.01383	0.01405	0.00066	1.010	5.583
19	0.015	0.01501	0.01363	0.01480	0.01365				
20	0.015	0.01352	0.01527	0.01339	0.01529				
21	0.015	0.01385	0.01504	0.01367	0.01506	0.01418	0.00073	2.290	1.915
3	0.025	0.02110	0.02299	0.02128	0.02299				
4	0.025	0.02138	0.02447	0.02138	0.02471				
5	0.025	0.02237	0.02035	0.02245	0.02043	0.02221	0.00153	1.092	0.482
11	0.025	0.02464	0.02417	0.02468	0.02412				
12	0.025	0.02480	0.02312	0.02475	0.02310				
13	0.025	0.02322	0.02384	0.02338	0.02387	0.02398	0.00067	0.993	10.414
19	0.025	0.02478	0.02363	0.02479	0.02367				
20	0.025	0.02348	0.02498	0.02322	0.02500				
21	0.025	0.02364	0.02485	0.02346	0.02479	0.02407	0.00070	2.364	1.924

The data shows that the tin-plated panels maintained line definition as well as the tin-lead plated panels. Some variation in the results was due to parameters outside this evaluation. These will be evaluated in subsequent line/space evaluations.

2. Panels 6-8, 14-16, and 22-24 were run through the hot air solder leveler (HASL) and solderability testing was performed (two coupons per panel). Table 4 displays the results.

Both the tin and tin-lead processes had one hole with a small pinhole in the solder. Otherwise, both processes performed similarly.

Accomplishments

The tin-lead electroplating process was replaced with a tin electroplating process. At the same time we switched tin-lead strippers and eliminated thiourea, a known carcinogen, from the plating shop. The change to tin electroplating also allowed us to eliminate two chemicals used in subsequent processes, our pumice scrub cleaner and our solder

conditioner. A rough cost estimate based on these reductions is shown in Table 5. A reduction in cost of nonconformance due to defects in the tin-lead electroplating/stripping operations may be realized in FY95.

Future Work

The only remaining source of lead in the Printed Circuit Boards Fabrication Department is from the hot air solder leveling (HASL) operation. An evaluation is currently under way to eliminate HASL and to supply boards to our customers using organic coatings. The coatings will protect the copper circuitry prior to next assembly use. This work is also being conducted under a production capability assurance program.

Table 4. Hot Air Solder Leveler and Solderability Testing Results

Panel/Coupon	Holes Tested	Holes Rejected	Comments
6/A	15	0	
6/B	15	0	
7/A	15	0	
7/B	15	1	pinhole in one hole
8/A	15	0	
8/B	15	0	
14/A	15	0	
14/B	15	2	pinhole in one hole, one hole rough
15/A	15	0	
15/B	15	0	
16/A	15	0	
16/B	15	0	
22/A	15	0	
22/B	15	0	
23/A	15	0	
23/B	15	0	
24/A	15	0	
24/B	15	0	

Table 5. Estimated Cost Reductions

Tin-Lead Processing Chemicals (FY94)					
	Material Volume	Material Cost	Waste Volume	Disposal Cost	Total Cost
Solderex LPC Makeup	293 gal	\$3,926	3785 lb	\$1,400	\$5,327
Solderex LPC Starter	143 gal	\$3,313			\$3,313
Solderex LPC Replen.	50 gal	\$1,163			\$1,163
Stannous Fluoborate	798 lb	\$3,567			\$3,567
Lead Fluoborate	279 lb	\$494			\$494
Fluoboric Acid	577 lb	\$739			\$739
Boric Acid	50 lb	\$210			\$210
En-Strip TL-106	884 gal	\$11,421	2587 lb	\$957	\$12,378
PD-510 Solder Cond.	106 gal	\$893	6815 lb	\$2,522	\$3,414
Fremont 238 Cleaner	200 lb	\$106	200 lb	\$74	\$180
					<u>\$30,784</u>
Tin Processing Chemicals (FY95 Estimate)					
	Material Volume	Material Cost	Waste Volume	Disposal Cost	Total Cost
Tin-Brite III Makeup	50 gal	\$902	3500 lb	\$1,295	\$2,197
Tin-Brite III Replen.	25 gal	\$893			\$893
Sulfuric Acid	1243 lb	\$1,032			\$1,032
Stannous Sulfate	100 lb	\$447			\$447
Sol-Strip 150	330 gal	\$2,666	900 lb	\$333	\$2,999
					<u>\$7,568</u>

Appendix A
Tin-Lead Plating/Stripping Process Flow

TIN-LEAD PLATING/STRIPPING PROCESS FLOW

TIN PLATING/STRIPPING PROCESS FLOW

Appendix B

XPS Results

Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #1
 Run: HC0228 Reg: 1 (WIDE) Scan: 1 Base Cps: 2391 Max Cps: 234689

Run: HC0212 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #1

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	497.90	0.56	1107.	7.20	118.69	4.45	0.047:1	8.01	
CU2P	936.50	3.40	20788.	6.30	63.54	95.55	1.000:1	91.99	

Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #2
 Run:HC0229 Reg: 1 (WIDE) Scan: 1 Base Cps: 3510 Max Cps:329741

Run: HC0213 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #2

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	496.60	0.32	1798.	7.20	118.69	3.22	0.033:1	5.85	
CU2P	933.80	2.48	47325.	6.30	63.54	96.78	1.000:1	94.15	

Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #3
 Run:HC0230 Reg: 1 (WIDE) Scan: 1 Base Cps: 2001 Max Cps:226910

Run: HC0214 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #3

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	489.50	1.12	1377.	7.20	118.69	3.42	0.035:1	6.20	
CU2P	936.20	2.36	34075.	6.30	63.54	96.58	1.000:1	93.80	

Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #4
 Run:HC0231 Reg: 1 (WIDE) Scan: 1 Base Cps: 3845 Max Cps:257456

Run: HC0215 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: CONTROL #4

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	499.00	0.24	1211.	7.20	118.69	4.59	0.048:1	8.24	
CU2P	936.60	2.47	22041.	6.30	63.54	95.41	1.000:1	91.76	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #1
 Run: 0115 Peg: 1 (WIDE) Scan: 1 Base Cps: 4716 Max Cps:529331

Run: HC0200 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #1

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	499.20	0.73	1222.	7.20	118.69	1.77	0.018:1	3.25	
CU2P	936.90	3.02	59370.	6.30	63.54	98.23	1.000:1	96.75	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #2
 Run: -00217 Reg: 1 (WIDE) Scan: 1 Base Cps: 4411 Max Cps: 486454

Run: HC0201 Scan: 1

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #2

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	497.40	0.37	1797.	7.20	118.69	2.90	0.030:1	5.28	
CU2P	938.60	4.43	52660.	6.30	63.54	97.10	1.000:1	94.72	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #3
 Run: HC0213 Reg: 1 (WIDE) Scan: 1 Base Cps: 3412 Max Cps:410184

Run: HC0202 Scan: 1

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #3

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	499.40	0.36	602.	7.20	118.69	1.86	0.019:1	3.41	
CU2P	936.90	1.77	27856.	6.30	63.54	98.14	1.000:1	96.59	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #4
 Run: HC0219 Reg: 1 (WIDE) Scan: 1 Base Ops: 5333 Max Ops: 561964

Run: HC0203 Scan: 1

Title: LTR 309504 - PRINTED CIRCUIT BRD: ELECTRO CHEMICALS #4

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	498.50	0.24	1208.	7.20	118.69	2.19	0.022:1	4.02	
CU2P	936.80	3.08	47160.	6.30	63.54	97.81	1.000:1	95.98	

Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #1
 Run: HC0220 Reg: 1 (WIDE) Scan: 1 Base Cps: 2369 Max Cps: 233741

Run: HC0204 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #1

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	488.80	1.98	3382.	7.20	118.69	27.45	0.378:1	41.40	
CU2P	937.70	0.15	7822.	6.30	63.54	72.55	1.000:1	58.60	

Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #2
 Run: HC0221 Reg: 1 (WIDE) Scan: 1 Base Cps: 2274 Max Cps: 274342

Run: HC0205 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #2

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	489.00	1.87	7646.	7.20	118.69	25.06	0.334:1	38.45	
CU2P	938.20	2.48	20009.	6.30	63.54	74.94	1.000:1	61.55	

Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #3
 Run:HC0222 Reg: 1 (WIDE) Scan: 1 Base Cps: 2690 Max Cps:292365

Run: HC0206 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #3

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	489.20	2.30	11796.	7.20	118.69	31.62	0.462:1	46.34	
CU2P	937.60	2.43	22323.	6.30	63.54	68.38	1.000:1	53.66	

Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #4

Run:HC0223 Reg: 1 (WIDE) Scan: 1 Base Cps: 2561 Max Cps:282689

Run: HC0207 Scan: 1

Title: LTR 309504 - PRINTED CIRCUIT BRD: MAC DERMID #4

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	488.80	2.14	9635.	7.20	118.69	26.38	0.358:1	40.10	
CU2P	935.50	3.26	23524.	6.30	63.54	73.62	1.000:1	59.90	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #1
 Run: HC0224 Reg: 1 (WIDE) Scan: 1 Base Cps: 1407 Max Cps: 178910

Run: HC0208 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #1

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	↓ Ratio	Mass conc %	Fit coeff
SN3D	488.50	1.70	5054.	7.20	118.69	7.17	0.077:1	12.60	
CU2P	936.30	3.77	57285.	6.30	63.54	92.83	1.000:1	87.40	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #2
 Run: HC0225 Reg: 1 (WIDE) Scan: 1 Base Cps: 3234 Max Cps:367686

Run: HC0209 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #2

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	488.90	1.63	6064.	7.20	118.69	12.00	0.136:1	20.30	
CU2P	936.80	2.98	38911.	6.30	63.54	88.00	1.000:1	79.70	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #3
 Run:HC0226 Reg: 1 (WIDE) Scan: 1 Base Cps: 3454 Max Cps:358769

Run: HC0210 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #3

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	489.10	1.67	6288.	7.20	118.69	9.99	0.111:1	17.18	
CU2P	937.50	3.65	49558.	6.30	63.54	90.01	1.000:1	82.82	

Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #4
 Run:HC0227 Reg: 1 (WIDE) Scan: 1 Base Cps: 4038 Max Cps:391212

Run: HC0211 Scan: 1
 Title: LTR 309504 - PRINTED CIRCUIT BRD: ENTHANE #4

Element	Position (eV)	Width (eV)	Area	Quant Factor	Atomic Mass	Atomic conc %	Ratio	Mass conc %	Fit coeff
SN3D	488.90	1.82	9400.	7.20	118.69	13.87	0.161:1	23.13	
CU2P	936.60	2.15	51075.	6.30	63.54	86.13	1.000:1	76.87	

Appendix C
Tin Electroplating TMS Data

TIN ELECTROPLATING TMS DATA

Panel	Nominal	Front Side	Back Side	Avg. Front	Avg. Back	Std.Front	Std.Back	CpFront	CpBack	CpK _{LSL} (Front)	CpK _{LSL} (Back)
3	0.005	0.00234	0.00420								
3	0.005	0.00254	0.00424								
3	0.005	0.00255	0.00404	0.00248	0.00416	0.00012	0.000106	5.628	6.299	-1.473	3.654
3	0.010	0.00754	0.00855								
3	0.010	0.00730	0.00861								
3	0.010	0.00711	0.00818	0.00732	0.00845	0.00021	0.000233	7.786	7.157	3.609	4.933
3	0.015	0.01213	0.01348								
3	0.015	0.01183	0.01314								
3	0.015	0.01210	0.01303	0.01202	0.01322	0.00017	0.000235	10.087	7.105	4.075	4.571
3	0.025	0.02143	0.02302								
3	0.025	0.02132	0.02296								
3	0.025	0.02110	0.02299	0.02128	0.02299	0.00017	3E-05	4.959	55.556	2.546	33.222
4	0.005	0.00231	0.00587								
4	0.005	0.00240	0.00590								
4	0.005	0.00227	0.00589	0.00233	0.00589	0.00007	1.53E-05	10.013	43.644	-3.371	62.992
4	0.010	0.00731	0.01013								
4	0.010	0.00719	0.01014								
4	0.010	0.00750	0.01024	0.00733	0.01017	0.00016	6.08E-05	10.662	27.400	4.976	28.331
4	0.015	0.01212	0.01477								
4	0.015	0.01181	0.01479								
4	0.015	0.01212	0.01505	0.01202	0.01487	0.00018	0.000156	9.312	10.670	3.756	10.392
4	0.025	0.02148	0.02499								
4	0.025	0.02127	0.02467								
4	0.025	0.02138	0.02447	0.02138	0.02471	0.00011	0.000262	7.934	6.354	4.369	5.986
5	0.005	0.00345	0.00293								
5	0.005	0.00350	0.00225								
5	0.005	0.00427	0.00250	0.00374	0.00256	0.00046	0.000344	1.450	1.938	0.537	-0.426
5	0.010	0.00846	0.00663								
5	0.010	0.00804	0.00645								
5	0.010	0.00858	0.00678	0.00836	0.00662	0.00028	0.000165	5.878	10.087	3.950	3.268
5	0.015	0.01354	0.01089								
5	0.015	0.01285	0.01082								
5	0.015	0.01319	0.01085	0.01319	0.01085	0.00035	3.51E-05	4.831	47.458	3.085	8.099
5	0.025	0.02264	0.02035								
5	0.025	0.02233	0.02058								
5	0.025	0.02237	0.02035	0.02245	0.02043	0.00017	0.000133	4.942	12.551	4.837	1.071
11	0.005	0.00426	0.00091								
11	0.005	0.00439	0.00191								
11	0.005	0.00400	0.00181	0.00422	0.00154	0.00020	0.000551	3.357	1.210	2.042	-0.882
11	0.010	0.01008	0.00958								
11	0.010	0.01008	0.00949								
11	0.010	0.00997	0.00929	0.01004	0.00945	0.00006	0.000148	26.243	11.228	26.471	10.001
11	0.015	0.01500	0.01381								
11	0.015	0.01469	0.01414								
11	0.015	0.01495	0.01406	0.01488	0.01400	0.00017	0.000172	10.014	9.682	9.774	7.752
11	0.025	0.02469	0.02424								
11	0.025	0.02472	0.02395								
11	0.025	0.02464	0.02417	0.02468	0.02412	0.00004	0.000151	20.620	11.014	38.627	9.075
12	0.005	0.00404	0.00235								
12	0.005	0.00413	0.00223								
12	0.005	0.00585	0.00222	0.00467	0.00227	0.00102	7.23E-05	0.654	9.216	0.547	-3.379
12	0.010	0.01038	0.00860								
12	0.010	0.01005	0.00861								
12	0.010	0.00978	0.00891	0.01007	0.00871	0.00030	0.000176	5.546	9.461	5.624	7.014

12	0 015	0.01507	0.01329									
12	0 015	0.01445	0.01333									
12	0 015	0.01488	0.01326	0.01480	0.01329	0.00032	3.51E-05	5.247	47.458	5.037	31.259	
12	0 025	0.02473	0.02310									
12	0 025	0.02472	0.02307									
12	0 025	0.02480	0.02312	0.02475	0.02310	0.00004	2.52E-05	19.118	66.227	36.324	41.016	
13	0 005	0.00218	0.00416									
13	0 005	0.00214	0.00403									
13	0 005	0.00196	0.00450	0.00209	0.00423	0.00012	0.000243	5.689	2.747	-2.579	1.689	
13	0 010	0.00845	0.00892									
13	0 010	0.00830	0.00891									
13	0 010	0.00848	0.00903	0.00841	0.00895	0.00010	6.66E-05	17.283	25.031	11.787	19.791	
13	0 015	0.01376	0.01383									
13	0 015	0.01319	0.01382									
13	0 015	0.01355	0.01384	0.01350	0.01383	0.00029	1E-05	5.782	166.667	4.047	127.667	
13	0 025	0.02341	0.02387									
13	0 025	0.02352	0.02390									
13	0 025	0.02322	0.02384	0.02338	0.02387	0.00015	3E-05	5.431	55.556	7.431	43.000	
19	0 005	0.00436	0.00191									
19	0 005	0.00468	0.00196									
19	0 005	0.00455	0.00195	0.00453	0.00194	0.00016	2.65E-05	4.142	25.198	3.169	-13.355	
19	0 010	0.00999	0.00889									
19	0 010	0.01002	0.00864									
19	0 010	0.01022	0.00868	0.01008	0.00874	0.00013	0.000134	13.330	12.411	13.534	9.275	
19	0 015	0.01484	0.01371									
19	0 015	0.01454	0.01360									
19	0 015	0.01501	0.01363	0.01480	0.01365	0.00024	5.69E-05	7.003	29.311	6.719	21.377	
19	0 025	0.02487	0.02371									
19	0 025	0.02473	0.02366									
19	0 025	0.02478	0.02363	0.02479	0.02367	0.00007	4.04E-05	11.746	41.239	22.521	30.242	
20	0 005	0.00222	0.00494									
20	0 005	0.00224	0.00512									
20	0 005	0.00224	0.00506	0.00223	0.00504	0.00001	9.17E-05	57.735	7.274	-22.132	7.419	
20	0 010	0.00871	0.01059									
20	0 010	0.00837	0.01065									
20	0 010	0.00831	0.01110	0.00846	0.01078	0.00022	0.000279	7.726	5.979	5.352	6.912	
20	0 015	0.01354	0.01532									
20	0 015	0.01311	0.01527									
20	0 015	0.01352	0.01527	0.01339	0.01529	0.00024	2.89E-05	6.867	57.735	4.656	61.045	
20	0 025	0.02316	0.02492									
20	0 025	0.02302	0.02509									
20	0 025	0.02348	0.02498	0.02322	0.02500	0.00024	8.62E-05	3.534	19.331	4.552	19.318	
21	0 005	0.00214	0.00533									
21	0 005	0.00222	0.00540									
21	0 005	0.00225	0.00539	0.00220	0.00537	0.00006	3.79E-05	11.724	17.609	-4.670	20.896	
21	0 010	0.00902	0.01010									
21	0 010	0.00891	0.01027									
21	0 010	0.00879	0.01055	0.00891	0.01031	0.00012	0.000227	14.488	7.335	11.320	7.785	
21	0 015	0.01380	0.01502									
21	0 015	0.01336	0.01512									
21	0 015	0.01385	0.01504	0.01367	0.01506	0.00027	5.29E-05	6.181	31.497	4.537	31.875	
21	0 025	0.02334	0.02470									
21	0 025	0.02339	0.02483									
21	0 025	0.02364	0.02485	0.02346	0.02479	0.00016	8.14E-05	5.185	20.464	7.169	19.618	