Appendix

A. Determination of copper concentration in methanol using ICP-OES

(i) Table I: Magnitude of electrical current measured during seasoning period (Fig. 4.4 (a)).

	Time (minutes)	Current (mA)
	0	1.9
	15	1.8
	30	1.6
	45	1.6
	60	1.5
	75	1.8
	90	2.0
	Average	**1.7**

(ii) Comparison between the copper concentration in methanol measured by ICP-OES with calculated copper concentration in methanol (Fig. 4.4 (b)).

Average leakage current, I : 0.0017A

Electrolysis period, t : 90 min.

Initial methanol volume, V_i = 1.0 liter, final methanol volume, V_f:= 0.5 liter

According to

a. First Faraday's Law of electrolysis

The mass of any substance liberated from an electrolyte by the passage of current is proportional to the product of the current and the time for which it flows.

By assuming the volume of methanol decreasing linearly (V_i : 1.0 L at t = 0s, V_f : 0.5 L at t = 5400s.), the estimated volume of methanol at time t, V_t

$$V_t = V_i - \left(\frac{V_i - V_f}{5400}\right)t$$

$$= 1 - \left(\frac{1-0.5}{5400}\right)t$$

$$= \frac{10{,}800 - t}{10{,}800}$$

∴ The estimated copper concentration in methanol at time t is

$$\left[Cu^{2+}\right] = \frac{W}{V_t}$$

$$= \frac{Itm}{2eN_A V_t}$$

$$= \left(\frac{t}{V_t}\right)\frac{mI}{2eN_A}$$

$$= \left(\frac{t}{10{,}800 - t}\right)\left(\frac{10{,}800x63.5x0.0017}{2x1.6x10^{-19}x6.023x10^{23}}\right)$$

$$= 6.05\left(\frac{t}{10{,}800 - t}\right) \text{ mg/liter or ppma}$$

Table II: Comparison between measured and calculated copper concentration in methanol (Fig. 4.4 (b))

Time (min)	Estimate copper concentration C1 (±0.1 ppma)	Measured copper concentration E1 (±0.1 ppma)	E2 (0.1 ±ppma)
0	0.0	0.7	0.0
15	0.6	1.6	0.9
30	1.2	2.5	1.8
45	2.0	3.2	2.4
60	3.0	4.1	3.4
75	4.3	4.8	4.1
90	6.1	5.5	4.7

Legends

E 1: Copper concentration in methanol measures using ICP-OES.

E 2: Copper concentration level in the methanol after subtracting the residual copper in the methanol at t = 0.

C 1: Calculated copper concentration.

(iii) Relationship between copper concentration in methanol and magnitude of current during copper decoration process (Fig. 4.5)

Table III: Results of copper concentration of methanol vs. magnitude of current

Time (min.)	Copper concentration of methanol (±0.1 ppma)	
	I: 3 mA	I : 20 mA
0	0.3	0.9
15	2.2	3.1
30	2.9	4.4
45	3.1	5.4
60	3.8	7.5

B: Studying distribution of copper dots size on copper decorated wafers (Fig. 4.8)

Table IV: Size of coper dots measured on wafer A (n=63)

	Area (±1 um^2)		Area (±1 um^2)		Area (±1 um^2)		Area (±1 um^2)
1	3,952	21	4,431	41	5,310	61	5,104
2	4,182	22	8,091	42	3,203	62	7,585
3	5,976	23	2,624	43	4,426	63	5,459
4	5,042	24	4,158	44	4,539	64	
5	2,838	25	3,739	45	2,221	65	
6	3,933	26	4,702	46	2,605	66	
7	4,220	27	13,950	47	2,916	67	
8	3,809	28	6,344	48	2,118	68	
9	4,169	29	4,266	49	2,297	69	
10	4,418	30	3,579	50	4,123	70	
11	2,037	31	4,564	51	3,809	71	
12	3,398	32	4,894	52	4,680	72	
13	4,288	33	4,358	53	2,784	73	
14	3,490	34	4,821	54	3,484	74	
15	3,216	35	4,734	55	3,138	75	
16	4,085	36	2,797	56	3,584	76	
17	3,963	37	5,881	57	4,764	77	
18	4,296	38	3,419	58	3,706	78	
19	5,299	39	3,579	59	3,649	79	
20	3,457	40	3,571	60	3,836	80	

Table V: Size of coper dots measured on wafer B (n=218)

	Area (±1 um²)		Area (±1 um²)		Area (±1 um²)		Area (±1 um²)		Area (±1 um²)
1	76063	51	7094	101	43505	151	45433	201	51438
2	87592	52	68451	102	54039	152	71694	202	60255
3	64182	53	29465	103	71052	153	64825	203	63439
4	35521	54	58920	104	57052	154	63279	204	45593
5	68260	55	60979	105	66070	155	56701	205	36223
6	78774	56	83334	106	41462	156	55325	206	63419
7	70339	57	85744	107	68179	157	64213	207	118824
8	61672	58	28682	108	57594	158	54150	208	25719
9	84448	59	80100	109	49731	159	20527	209	54290
10	38333	60	91097	110	59372	160	20678	210	57227
11	48074	61	74988	111	54059	161	16932	211	13738
12	6949	62	70640	112	59734	162	59493	212	11498
13	49108	63	55906	113	62626	163	57725	213	31835
14	42610	64	83514	114	57323	164	55716	214	52231
15	13578	65	80100	115	60878	165	38935	215	43303
16	53738	66	68189	116	65448	166	65167	216	62816
17	67426	67	26302	117	61270	167	45493	217	20788
18	62465	68	76585	118	79447	168	105608	218	35721
19	44027	69	74366	119	105016	169	164036		
20	56209	70	46377	120	72156	170	200150		
21	74906	71	84217	121	45413	171	67195		
22	57072	72	20417	122	81596	172	60055		
23	78252	73	94300	123	75531	173	53397		
24	73271	74	49852	124	85463	174	42731		
25	20055	75	86377	125	81094	175	15004		
26	105116	76	54813	126	75229	176	52362		
27	58066	77	70620	127	59513	177	67657		
28	14932	78	82862	128	83705	178	69445		
29	71001	79	67808	129	71664	179	81325		
30	77790	80	67496	130	56018	180	35852		
31	62435	81	70720	131	50905	181	56084		
32	59754	82	66924	132	76886	182	84458		
33	52101	83	97262	133	54140	183	75440		
34	19101	84	69997	134	50324	184	63951		
35	57233	85	99583	135	73703	185	48033		
36	56048	86	63720	136	56259	186	65257		
37	62638	87	38350	137	51097	187	58397		
38	66000	88	77288	138	75480	188	62344		
39	65910	89	34848	139	50223	189	65066		
40	30319	90	102053	140	35511	190	58679		
41	56650	91	82259	141	70057	191	58176		

42	102646	92	69806	142	54923	192	63077		
43	51037	93	66773	143	74627	193	61641		
44	89731	94	66422	144	39116	194	56760		
45	9430	95	74556	145	82149	195	58468		
46	97052	96	80472	146	60477	196	56660		
47	27175	97	64865	147	18197	197	63780		
48	50635	98	61129	148	71524	198	27275		
49	72719	99	73241	149	70077	199	24283		
50	72056	100	36706	150	26121	200	56098		

C: Studying the impact of size of D-defect on the size of copper dots (Fig. 4.10)

Table VI: Relationship between size of copper dots and size of D-defects

Relationship between size of copper dots vs. size of D-defects

	Area of Cu dot (±1 um^2)	Area of D-defect (±1 nm^2)
1	87340	15086
2	85292	23449
3	77529	31484
4	71222	48066
5	70479	18916
6	70760	32741
7	69104	15967
8	67818	11995
9	65437	11868
10	64363	42660
11	57433	13822
12	50966	11876
13	49841	15671
14	21410	6082
15	16259	16870

D: Determination of stressed field by V_{ox}/V_{app} ratio measurement (Fig. 4.19)

Table VI: Relationship of V_{ox}/V_{app} as a function of proble exposed length

V_{app} (V)	V_{ox} (V)					
	l: 1.0 mm		l: 1.5 mm		l: 2.0 mm	
	Ave	Std	Ave	Std	Ave	Std
3	2.4	0.01	2.5	0.02	2.5	0.01
6	5.1	0.04	5.2	0.04	5.3	0.02
9	7.8	0.01	7.9	0.06	8.1	0.02
12	10.4	0.03	10.6	0.12	10.9	0.01
15	12.9	0.08	13.3	0.21	13.6	0.04
18	15.5	0.12	15.9	0.31	16.3	0.12
21	18.0	0.28	18.4	0.15	18.9	0.19
24	20.3	0.25	20.6	0.48	21.3	0.18

E: Effects of copper concentration on the conductivity of methanol (Fig. 4.21)

Table VII: Camparison between measured and calculated conductivity of methanol

Copper concentration in methanol		Conductivity of methanol	
ppm = mg/liter	**micro-mol/liter**	**Calculated (micro Siemen)**	**Measured (micro Siemen)**
0.0			0.5
0.3	4.9	0.9	2.2
0.5	7.2	1.0	3.7
2.2	35.3	3.1	3.4
2.9	45.2	3.9	4.4
3.1	48.5	4.1	4.2
3.1	49.4	4.2	5.4
3.2	50.4	4.3	4.1
3.8	60.0	5.0	6.6
3.8	60.1	5.0	4.4
4.1	65.0	5.3	4.6
4.4	68.8	5.6	6.4
5.4	85.6	6.9	8.5
6.4	100.9	8.0	4.9
7.5	118.1	9.3	11.9