Copper Foil Characterization and Cleanliness Testing

By I. Artaki, M. H. Papalaski and A. L. Moore

During implementation of SPC concepts in circuit inner layer manufacturing, it was noted that variations in copper foil characteristics can contribute to variations in process control and quality. Two critical characteristics were identified: (1) cleanability of the vendor-applied chromate passivation treatment and (2) copper crystal orientation, which affects the sidewall geometry of circuit paths. Among screening methods evaluated for SPC of cleanability, a surface monitor based on the photoelectric effect was found to be the most efficient and reliable. The effect of crystal orientation on etch performance affected only line circuits with a width of three mils or less, and only when the circuit features are generated under controlled-process conditions.

Manufacturing processes for printed wiring boards primarily use "subtractive" technology during fabrication. A hardboard panel in multi-layer, double-sided rigid or inner-layer form starts its process completely clad with copper foil. From here, the process follows one of two basic paths: (1) print and etch or (2) print, plate and etch. Depending on the path, the copper is subjected to various surface preparation coating and/or plating operations. In each case, a significant portion of copper is etched away or removed from the structure; thus, the technology is termed subtractive. In either case, interaction occurs between the copper and the fabrication processes.

Properties of the copper and those of the dielectric material between circuit traces and layers obviously dictate the characteristics of the final board structure and must meet end-point specifications. Interactions are encountered with almost every step in the process sequence. Because there are multiple processes, each with variations, the characteristics of copper that relate to every process is not well understood. This is particularly evident as new different processes are introduced to meet ever-changing end-product requirements.

During inner-layer development and implementation of statistical process control (SPC), variations in characteristics of foil that clads inner-layer laminate can contribute to variations in process performance and quality. This problem has received publicity and some activity in the industry. Improved cleaning processes have been responsive, but costly. An optimum cleaning sequence has been developed and implemented in the inner-layer process area, AT&T Richmond.

Variations in copper foil that relate to inner-layer manufacturing affect cleanability and final etching. The primary concern of cleaning is the removal of the chromate stain-proofing coating applied to the foil in its final stage of manufacture. The application of the coating is a dynamic and sometimes uncontrolled process, based on observations and data collected from samples from four major suppliers, monitored as a function of time over the past 3 years. The chromate level measured by X-ray photoelectron spectroscopy (XPS) can vary from a level easily cleaned with a light microetch to high levels in localized spotted areas that are virtually impossible to clean. Unremoved chromate inhibits micro etching of copper and can compromise photo resist adhesion by inhibiting generation of optimum topography and by limiting chemical bonding capabilities of the photo resist. Adhesion bonding promoters in photo resists are intended for bonds to copper, not to chromium compounds. Although the chemical cleaning sequence at AT&T Richmond has been tailored to remove all normal quantities of chromate[1] the ability to remove heavy spots adequately has not been demonstrated. Furthermore, local heavy areas are impossible to detect visually. In inner-layer final etching, variations in etch rates and etch factors can be examined as a function of foil crystal structure[2]. Etch factor is defined as the ratio of the rate at which the material is etched downward vs. the lateral rate. It influences the undercut geometry of the cross-section of the etched circuit. The importance of crystal structure increases as the circuit features become smaller and the degree of etching precision becomes more significant.

Elements of SPC have been implemented on several processes in the inner-layer process area at Richmond. Notable examples are the control of (1) coating thickness at the coat and print process, (2) the micro-etch rate or weight loss of the chemical cleaning operation and (3) the cupric chloride etch uniformity. These implementations have improved overall quality and yields to previously unachieved levels. Because of occasional difficulties in cleaning and processing due to variations of copper characteristics, it was determined advantageous to implement SPC concepts on copper foil manufacturing operations as well. SPC of incoming foil would be feasible if a simple screening test were available and if testing were executed soundly.

Table 1
Composition by XPS of Copper Surface Films*

Foil/ Condition	Cu	O	C	Cr	Zn	P	N
A/as-received	0.5	44. 5	43.3	3.1	8.5	-	-
B/as-received	1	44	38	3.5	11	-	1.7
C/as-received	1	44	42	1.6	10	-	-
D/as-received	-	57	30	0.5	2.7	9	-
A/cleaned	34	25	40	-	-	-	-
B/cleaned	26	23	50	-	-	-	-
C/cleaned	30	40	27	-	-	-	-
D/cleaned	9	54	27	2.7	-	6	-
A/baked**	49	31	20	-	-	-	-
B/baked**	47	38	14	-	-	-	-
C/baked**	55	27	17	-	-	-	-
D/baked**	6	59	24	3.7	-	6.3	-

* Numerical values in percent
**Cleaned 1 minute in acidic detergent after baking 3 hr at 177^{O}C.

Table 2
Results of Copper Cleanliness Testing

Foil/Condition	Cu by XPS (percent)	OSEE (OP1020)	Oven Test [a]	Polysulfide [b]
A/as received	0.5	17	1	1
B/as received	1	32	1	1
C/as received	1	35	1	1
D/as received	0	15	1	1
A/cleaned [b]	34	730	3	4
B/cleaned [b]	26	700	3	3
C/cleaned [b]	30	850	3	3
D/cleaned [b]	9	80	2	1

[a] Numbers based on a scale from 1 to 5
[b] Cleaned in AT&T standard pre-cleaning line

One project objective was to monitor (1) foil characteristics that affect cleanability and adhesion (e.g., chromate content) as a function of time and supplier batch and (2) crystalline structure as it influences etching. Another was to evaluate various screening methods, to determine if any would be suitable as an SPC check on incoming copper-clad material.

Stain-proof Treatment Removal And Copper Cleanliness Testing

In the past, inner layers inadequately cleaned by the standard pre-cleaning process were examined in localized areas for stain-proof coating residues. XPS was traditionally considered the method of choice for the detection of these residues. However, XPS is a highly sophisticated technique that doesn't lend itself to the analysis of a large number of specimens and would not be appropriate as an SPC method. It was apparent that a more practical procedure would be needed to distinguish acceptable from non-acceptable incoming material.

A "Surface Cleanability Task Group" has been established to identify a test method for assessing copper foil cleanability. AT&T has agreed to act as a test facility for the preliminary test program. A polysulfide test, an oven test and a back-etch method have been proposed. Details may be obtained through the IPC Foil Cleanability Subcommittee. Results will be made available through the I PC.

We have been investigating another test procedure that makes use of a non-destructive surface monitor * based on optically stimulated electron emission (OSEE),[3,4] whereby high energy ultraviolet radiation impinges on the metal surface and causes photo emission of electrons originating from the metallic surface or its top layer (oxide or other form of contamination). By using an appropriate wavelength of light, these surface species, depending on their own OSEE, will either enhance or attenuate the OSEE from the substrate. We have observed that organic contamination and the stain-proof coating attenuate the copper OSEE. The generated photoelectric current is in the picoampere range and is detected and displayed in digital format. Therefore, a reduction in the current reading corresponding to clean copper indicates the presence of contamination. The amount of reduction is dependent on the level of contamination.

*OP 1020, Photo Acoustic Technology, Inc., Westlake Village, CA

Two sets of specimens have been employed for evaluating the test procedure: (1) four copper foils (A through D) of known identity, laminated under the same conditions by an outside laminator and (2) unidentified copper foils (1 through 12) obtained from the IPC Surface Cleanability Task Group. XPS was employed as a reference because of its high sensitivity and accuracy. Table 1 summarizes XPS results after one minute of cleaning in an acidic detergent specifically formulated for removal of the chromate passivation layer and after a bake and clean sequence.

The composition of the passivation layer was similar on all foils, except for foil D, which showed the presence of phosphorous. After cleaning, relatively high concentrations of chromium and phosphorous remained on this foil. The total copper concentration was only 9 percent, compared to 26-34 percent on the other foils. This result was not a consistent condition specific to this foil. Based on data accumulated in the last two years, difficulty with removal of the passivation layer may be experienced with foil from any of the four suppliers. For this reason, SPC may be required on incoming material.

The results of two IPC tests and OSEE test data are compared in Table 2. To report the data, the copper content for each foil was used as the indicator of overall surface cleanliness. A low copper content was associated with the presence of contaminating

Table 3
Cleanliness Detection by OSEE

Process	Foil A	Foil B	Foil C	Foil D
No Cleaning	17	32	35	15
5 sec HCL	215	450	500	70
15 sec HCL	300	450	500	70
30 sec HCL	550	600	650	90
30 sec detergent	730	700	850	80

Table 4
Auger Analytical Data

Bake	Surface	Foil A	Foil B	Foil C	Foil D
None	As-received	29	45	20	47
None	Sputtered [a]	96	96	93	97
3 hr [b]	As-received	32	59	60	10
3 hr [b]	Sputtered [a]	95	97	96	-

[a] Sputtered to remove 25 Angstroms
[b] Baked at 177 °C

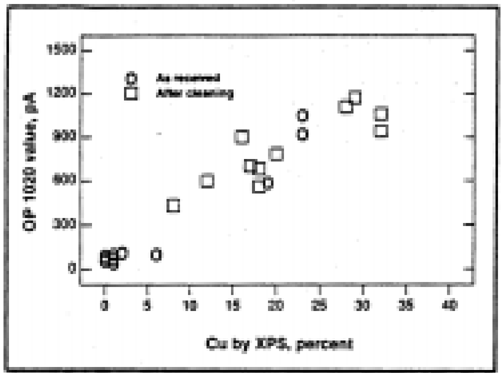

Fig. 1—OSEE (OP 1020) data as a function of the copper content determined by XPS.

species and insufficient cleaning. To evaluate the results of the polysulfide and oven-test methods, an arbitrary scale of 1 to 5 was used with1 representing poor and 5 indicating excellent uniformity of coverage. Values for the OSEE data also are relative, depending on the selected sensitivity factor, but are directly proportional to the electronic currents generated by the copper substrate. In this study, the current gain factor was set at 2.5.

The OSEE method shows the highest level of sensitivity to copper contamination. All methods detected the problem associated with foil D; however, the OSEE data correlated most closely with XPS data. The polysulfide and oven-test methods appear to be qualitative. After processing this batch of specimens through the standard precleaning line, the laminated D foils showed long, non-uniform streaks generally associated with uneven cleaning and micro-etching.

If the OSEE procedure is employed in a controlled mode and appropriately calibrated, it may provide a quantitative measurement of chemical cleanliness. Although this has not yet been fully explored, the data in Table 3 show promise. (With OSEE, 1-oz. copper, etched to l/2 oz., produced a reading of 1100.)

To preserve the dimensional stability of the laminate during inventory, suppliers often apply an additional post lamination bake of 3 hr at 177 °C. This practice raised concerns regarding the integrity and diffusion of the passivation layer. The results of XPS determinations (Table 1) show that, except for foil D, a higher level of cleanliness was achieved with such a bake, possibly due to decomposition or volatilization of material applied by the treatment.

To explore the possibility of passivation - material diffusion through the copper, Auger analysis was performed before and after sputtering 25 A from the surface. (The thickness of most passivation films is 25 A.) The essentially equal copper contents in Table 4 of the etched surface layers indicate that no diffusion took place as a result of baking. However, the increased copper concentration after baking indicates that the bake volatilized some passivation material and confirmed XPS data showing better cleanability after baking.

XPS data for 12 unidentified specimens provided by the IPC Surface Cleanability Task Group are presented in Tables 5 and 6. The foils were supplied by four vendors asked to provide a set of three foils treated with (1) the standard process, (2) an easy-to-remove or no passivation treatment and (3) a difficult-to-remove passivation film.

Table 5 XPS data indicate that specimens 2, 4 and 9 had not been treated, but films on the other specimens showed a wide composition range. Cleaning with HCl removed most of the films, except for foils 1, 6,10,11 and perhaps 12 (Table 6). There is a strong correlation (Fig. 1) between the OSEE and XPS data, neglecting Specimen 8.

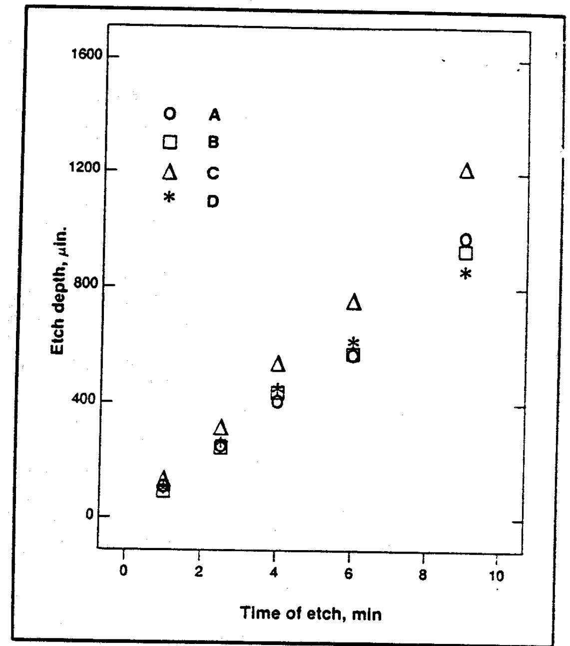

Fig. 2—Etch depth as a function of etching time.

The data above show that OSEE is capable of distinguishing acceptable from non-acceptable copper foil, and can quantitatively determine the level of cleanliness after cleaning. The method could be implemented as an SPC tool to screen incoming material. However, it is highly sensitive to low levels of contamination. For example, a decrease in the XPS copper content from 30 to 20 percent, which might correspond to a single mono layer of contamination, results in a decrease of the OSEE reading from 1100 to 600. To establish realistic pass/fail criteria and properly calibrate the instrument, the effect of such a low level of conversion coating residue on process performance needs to be understood and quantified.

Copper Morphology and Effect on Etch Performance

A specific crystal configuration is required to generate straight sidewall structures with little or no undercutting during etching.[2] Anisotropic etching with little line loss may be obtained from electroformed copper foil that has a large fraction of the crystal planes in the [111] direction.[2] It has essentially been shown also that there is a direct correspondence between the [111] content of the foil and copper hardness, which in turn is a function of grain size and rate of microetching. Thus, it can be predicted that foil that etches rapidly may have a high [111] configuration and will produce straight sidewalls with minimal line loss.

To confirm this prediction and characterize some foils of interest, several measurements were made. Etch rates with sodium persulfate were measured for each foil over the entire thickness of the 1-oz. foil. The fraction of crystal planes in the [111] orientation was determined by X-ray diffraction at five depth levels from the top down to the treated side bonded to the laminate. Small batches of each type of foil were processed through the standard print-etch sequence using a "fine-line" test vehicle' for circuit generation. Finally, the undercut or line- width loss was determined on cross-sectioned 3- and 6-mil-wide circuits.

Figure 2 compares the etch rates for four copper foils. Although there is some scatter, foil C etched at the fastest rate. The slow rate for foil D may be partly explained by the problem associated with the removal of the passivation film described previously. However, the reduction in rate observed below the

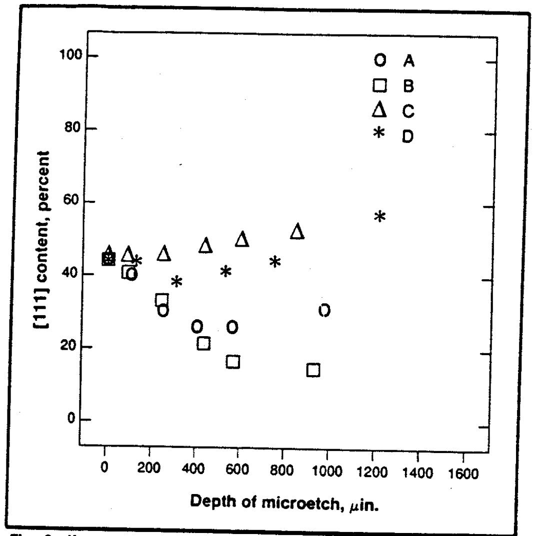

Fig. 3—X-ray diffraction data showing [111] content as a function of microetch depth.

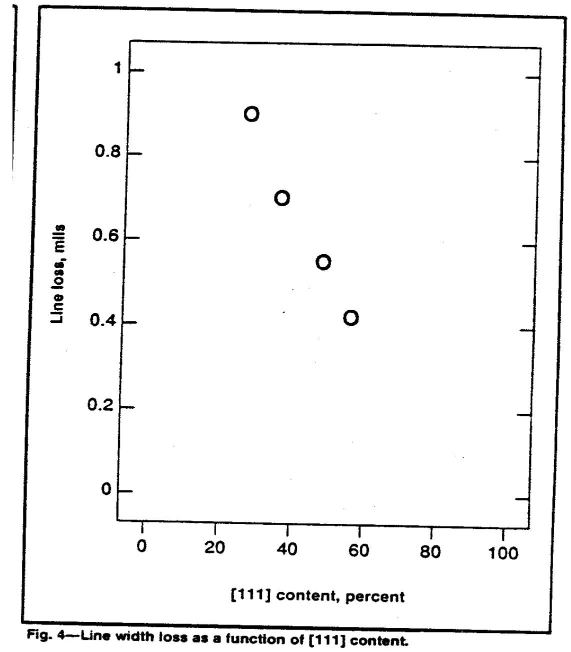

Fig. 4—Line width loss as a function of [111] content.

surface suggests that some other factor such as an impurity or diffusion of zinc or chromium into the bulk copper, may have an effect. Similar measurements over the past several years on other batches of foil showed that the etch rate of foils D and C were comparable. Foil B consistently etched at the slowest rate.

Figure 3 depicts the [111] content obtained by X-ray diffraction at five depth levels for foils A through D. This analysis has been performed on other batches of foils in the last two years and the trends have always been the same, suggesting that this may not be an area prone to as many uncontrolled process variations as noted for application of the passivation treatment.

TABLE 5
Surface Film Contamination by XPS[a]

Foil	C	O	Cr	Zn	P	Mg	Ca	Be	S	Si	Cu
1	23	52	5	4	10	-	1	-	-	-	6
2	27	50	-	-	-	-	-	-	-	-	23
3	15	43	-	12	12	-	2	16	-	-	1
4	31	46	-	-	-	-	-	-	-	-	23
5[b]	25	47	-	12	-	3	5	-	-	-	5.9
6	58	29	-	-	-	1.3	-	-	-	3.9	8
7	31	50	4	15	-	-	-	-	1.4	-	0
8	36	42	8	12	-	-	-	-	1.4	-	1
9	41	39	-	-	-	-	-	-	-	-	19
10	26	40	10	21	-	-	-	-	-	-	0
11	25	32	23	20	-	-	-	-	-	-	0
12	27	40	14	11	-	3	4	-	-	--	2

[a] Atomic percentage
[b] Foil 5 also contained 0.8 atomic percent boron

At the surface, all foils were equivalent in their crystal film orientation. This applies to [111], [200] and [220] orientations rate. During etching, the [111] content changed considerably however decaying rapidly to less than 20 percent in foil B, for example. The [111] content was steadier for foils C and D. In agreement with the predicted model, the etch rates of foils B and C followed the same trends, with foil B etching at the slower rate.

Based on X-ray data and the model described above, foil B would be expected to exhibit the greatest line-width loss.

Table 6
Surface Film Composition by XPS after Cleaning [a]

Foil	C	O	Cr	P	Cl	Mg	Sn	Cu
1	32	43	6	6	4	-	-	8
2	50	14	-	-	7	-	-	29
3	37	30	-	-	6	-	-	28
4	45	15	-	-	7	-	-	32
5	43	19	-	-	4	1	-	32
6	72	12	-	-	2	5	-	6
7	52	25	-	-	6	-	-	18
8	51	24	-	-	7	-	-	18
9	59	15	-	-	6	-	-	20
10	44	27	-	-	4	-	6	17
11	48	26	-	-	5	-	8	12
12	64	12	-	-	5	2	-	16

[a] Atomic percent after HCL cleaning

TABLE 7
Circuit Definition Capability

Foil	Line Width, mils	Resistance, ohms	Defects [a]
A	1.4	1.6	12
B	1.4	1.7	12
C	1.5	1.5	4
D	1.4	1.8	7

[a] Percentage of coupons that contained open circuits.

Line width loss measured on cross-sections of 3- and 6-mil circuits is indicated in Fig. 4, as a function of averaged [111] content for each foil. In this case, etching conditions were specifically set up for 3-mil lines, primarily to avoid unintentional over-etching. In a separate experiment with etch conditions optimized for a 6-mil lines, 3-mil lines were significantly over-etched. Table 7 summarizes the line-width and electrical-test measurements in this case. The over etch reduced the normal 3-mil lines to 1.4-1.5 mils and obscured any differences that might have been attributed to the structural characteristics of the foils. Both the line-width and resistance values show negligible variation among the foils included in this study. The defect rate, also shown in Table 7, indicates the percentage of coupons with open circuits resulting from the loss of photo resist adhesion or over-etching or both and probably reflects the combined effects of surface cleaning effectiveness and crystal orientation.

If a particular copper foil has a high [111] content, this benefit for line definition may not be realized unless the etching process is under control and the etching conditions are precisely optimized for fine-line definition. The copper crystal orientation is only one factor affecting the features of fine lines with a width of 3 mils or less. Relative to the [111] content the best and worst foils differ at most by 0.5 mil. This difference becomes negligible in the case of line widths of 4 mils or more. However, as the requirements for fine-line features become more stringent, the effect of copper crystal orientation on etch performance needs to be addressed and better understood in future fine-line development studies.

Conclusions

The ability to process inner layers with fine-circuit features can be influenced by characteristics of the copper foil used to start the process. The characteristic that has the most effect on adhesion is cleanability, which can be measured by a relatively simple instrumented procedure. A procedure based on Optically Stimulated Electron Emission was found to be efficient and reliable and should be considered as a tool for statistical process control of incoming material.

Crystal orientation of the copper can affect the etching rate and yield of fine circuit dimensions. Although much remains to be learned about the cleaning and etching characteristics of copper, implementation of SPC of the copper foil would be a sound step in reducing foil variability.

Acknowledgments

The authors thank Gary Heyer and Paul Sakach for performing the surface analysis described in this study.

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