Ni/Cr Alloy Stripper for Flexible Wiring Boards

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Abstract

For wiring boards used in electronic equipment, the demand for a flexible wiring board is increased due to its lightweight, thin features and flexibility. A typical construction of the flexible wiring board includes a polyimide film, used as an electrically insulating base material, a thin metal tiecoat, a copper seedcoat, and a layer of electrodeposited copper. The tiecoat metal is either chromium or nickel based alloy, which serves to enhance adhesion. The purpose of the copper seedcoat is to provide sufficient electrical conductivity to permit electroplating to the desired final copper thickness. Thereafter, the boards go through conventional processes of photoimaging, etching, and stripping to form fine line wiring boards.

The fine line wiring formation can be finished by a single step etching process that is involved in photoimaging, etching copper and Ni/Cr alloy together and then stripping the resist. The etching chemistries used for single step etching were typically cupric or ferric chloride/hydrochloric acid solution or permanganate acid solution. As a result of photoresist chemistry leaching into cupric or ferric chloride/hydrochloride acid etchant, the etch rate for Ni/Cr alloy would slow down, the process also had potential to cause too much dissolution of copper. For permanganate acid etchant, Ni/Cr etch rates slow due to passivation by MnO_2 reaction product, a 'Neutralization' step with oxalic acid or ascorbic acid to remove MnO_2 is necessary to maintain acceptable etch rates. To solve the issues in the single step etching, two-step etching was developed and discussed in the paper. Two-step etching involves in photoimaging, copper etching, resist stripping and then Ni/Cr alloy etching. Since Ni/Cr alloy is etched away post photoresist stripping, this etching process needs to be selective, removing the unwanted Ni/Cr alloy without attacking the copper circuits.

MacDermid has developed Eliminator NC process for this application. The process is an efficient stripper that dissolves the tiecoat metal, Ni/Cr alloy, which is sputtered on polyimide, without affecting on copper circuits. The Ni/Cr alloy removal rate depends on the etching solution temperature. At 45-50°C, the alloy can be removed within 30 seconds. Under such conditions, the etch rate on copper is only about 1.0-2.0 micro inch.

The process conditions and influential factors were also discussed in the paper, SEM and EDS were used to determine the removing degree of the Ni/Cr alloy.

Introduction

For wiring boards used in electronic equipment, the demand for a flexible wiring board is increased due to its lightweight, thin features and flexibility. Polyimide film based substrates are widely used in the applications. There are two approaches to produce the copper-polyimide laminate, adhesive process and direct metallization process. The adhesive approach, in which copper foil is bonded to polyimide film coated with an adhesive layer by applying heat and pressure, suffers some drawbacks, such as copper foil minimum thickness at 9-12 µm, thermal stability and other issues with the adhesive itself. The second approach is to deposit metal layer directly on the polyimide surface. A vacuum technique, such as sputter deposition, is used to produce a seed-layer metal, tiecoat metal and copper seedcoat, on polyimide film, the metal deposit is subsequently plated with a layer of electrodeposited copper. The sputter coated tiecoat metal, is either chromium or nickel based alloy, which serves to enhance adhesion. The purpose of the copper seedcoat is to provide sufficient electrical conductivity to permit electroplating to the desired final copper thickness. This approach is highly versatile, and copper thickness can be tailored to the application need, which is suitable for very minute wiring patterns at wire pitches of less than 30 μm.

Thereafter, the boards go through conventional processes of photoimaging, etching, and stripping to form fine line wiring boards. The fine line wiring formation can be finished by a single step etching process that involves in photoimaging, etching copper and Ni/Cr alloy together and then stripping resist.

The etching chemistries used for single step etching have traditionally comprised cupric or ferric chloride/hydrochloric acid solutions or permanganate acid solutions. With photoresist leaching into cupric or ferric chloride/hydrochloride acid etchant, the etch rate for Ni/Cr alloy is generally slowed down. The process also has the potential to cause too much dissolution of copper. For permanganate acid etchant, Ni/Cr etch slows due to passivation by the MnO_2 reaction product, and a step of "neutralization" with oxalic acid or ascorbic acid to remove MnO_2 is necessary to maintain good etch rates. To solve the issues resulting from single step etching, a two-step etching process is developed as discussed in the paper, in which the Ni/Cr alloy is etched after the photoresist is stripped. This process needs to be selective, such that the etching solution removes the unwanted Ni/Cr alloy without attacking the copper circuits.

Ni/Cr Alloy Tiecoat Etching Process

Due to the issues of photoresist leaching and too much dissolution of copper, a two-step etching process was developed. The whole process for circuit formation of polyimide flexible printed circuit is involved in several steps as described in figure 1 below.

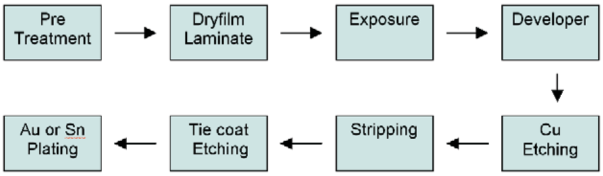

Figure 1. Circuit formation process for polyimide flexible boards

After the copper etching and resist stripping steps, circuits were formed with tie coat layer under copper as described in figure 2. The tiecoat layer, Ni/Cr alloy, need to be removed before final plating step.

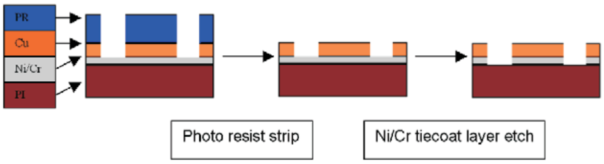

Figure 2. Typical construction of polyimide circuit formation

Since the copper surface has no resist to protect in the two-step etch process, the challenge for the removal of Ni/Cr tiecoat layer is that the chemical to remove the tiecoat has to be non-reactive to copper circuits. MacDermid has developed the process, ELIMINATOR NC, to meet the requirements. The process can etch away Ni/Cr alloy tiecoat within 1.0 min, while copper was etched only about 1.0-2.0 μinch during the process.

1. Bath Temperature

During the tiecoat layer etching process, the Ni/Cr alloy removal was monitored under microscope by checking (1). Ni/Cr alloy in a large area, (2). Ni/Cr alloy in the cross pattern on the board.

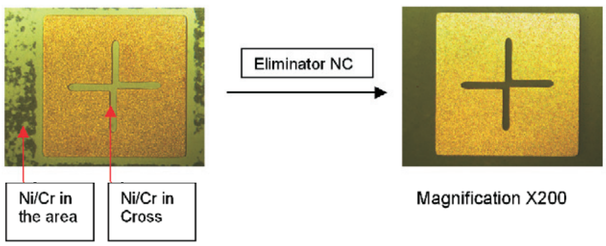

Figure 3. Cross pattern before and after Ni/Cr alloy removal

After these areas were cleaned, electron scanning microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to check fine lines.

The Ni/Cr alloy removal rate depends on the bath temperature, the alloy can be removed within 30 seconds when the temperature at 45-50 °C. Under such conditions, the etch rate on copper was only about 1.0-2.0 µinch. The chart on the relationship between the temperature and the time to remove alloy was shown below.

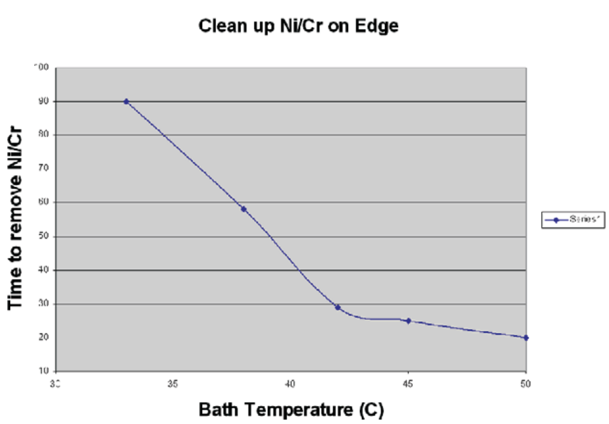

Figure 4. Ni/Cr alloy removal rate and bath temperature

2. Chemistry

There are three important factors in Eliminator NC stripping chemistry, acidity, chloride concentration and accelerator, NC 7582. The removing rate of Ni/Cr alloy layer is related to these three factors. DOE was used to study the influence of acidity, chloride and NC 7582 on Ni/Cr alloy removal rate.

Design factor: 1. Acidity, N
2. Chloride concentration, g/L
3. NC 7582 concentration, ml/L

Response: 1. Time to clean Ni/Cr on edge, second
2. Etch % of Ni/Cr alloy on the cross in 60 second

The experiments were done with bath temperature at 50 °C, variation on acidity, chloride concentration and accelerator, NC 7582. Ni/Cr alloy removal was monitored by checking (1). Time to etch away Ni/Cr alloy visually in a large area, (2). Ni/Cr alloy in the cross pattern etched percentage under microscope after parts were in the chemistry for 60 seconds.

DOE charts indicated that both acid and chloride concentration play important roles, the higher the acidity and the higher the chloride concentration, the faster the Ni/Cr was etched. The accelerator, NC 7582, can speed up Ni/Cr alloy etching rate under higher concentration, but the copper could be tarnished when too much NC 7582, above 150 ml/L, was used. DOE data showed NC 7582 at 100 ml/L can widely open the operation window for the process to remove Ni/Cr alloy.

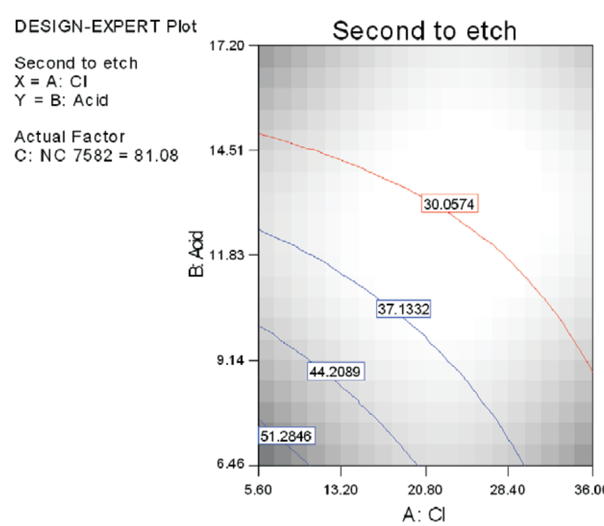

Figure 5. DOE on acidity and Cl concentration affecting on Ni/Cr removal

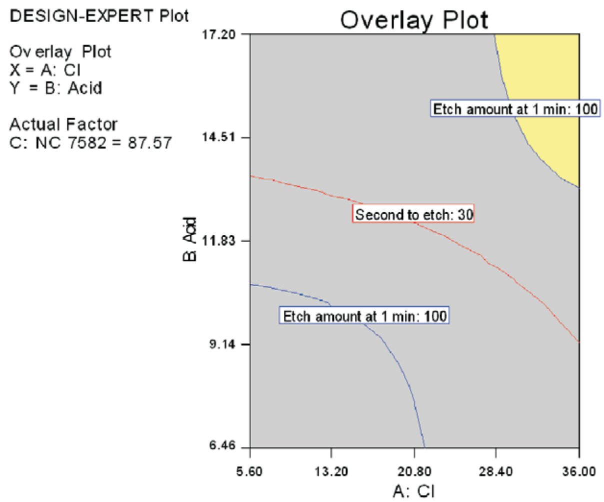

Figure 6. DOE conditions to remove Ni/Cr alloy within 30 seconds when NC 7582 was at 88 ml/L

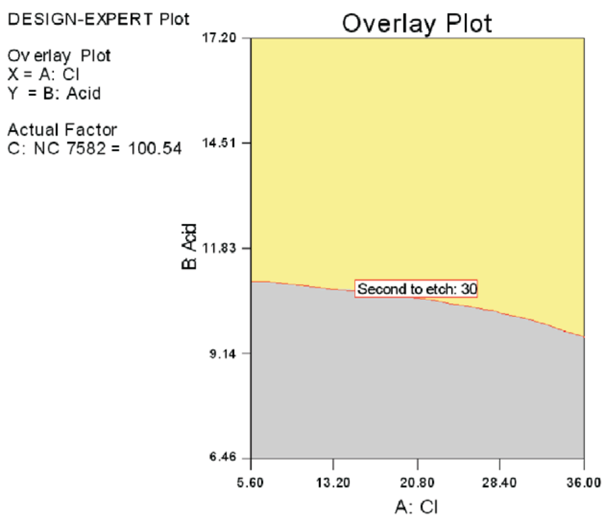

Figure 7. DOE conditions to remove Ni/Cr alloy within 30 seconds when NC 7582 was at 100 ml/L

3. Predip

As mentioned above, the chemical has almost no reactivity to copper, the etch rate to copper was at 1.0 to 2.0 μinch. If any excess copper leftover from copper etch process, it could not be removed from this process as shown below.

Figure 8. Cross pattern with excess copper before and after the process

In order to clean up some of the excess coppers leftover from copper etch process, a predip step by hydrochloric acid, 18%, was optionally put into the process to etch copper slightly in predip, 1-5 μinch, to reduce the defects caused by excess copper. The etch rate in predip depends on copper concentration in the predip HCl solution (18% HCl), as indicated in figure 9.

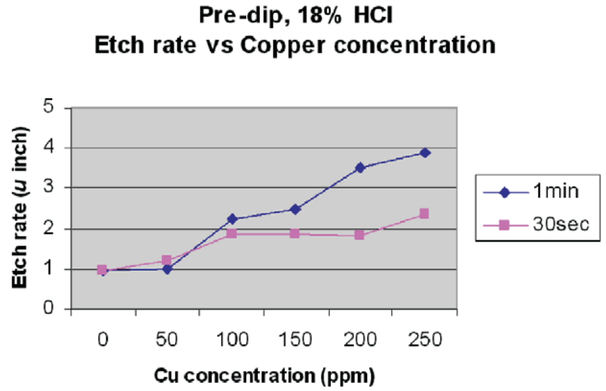

Figure 9. Copper etch rate in predip

Eliminator NC on Copper Fine Lines

SEM and EDS were used to determine any Ni/Cr residue near copper trace.

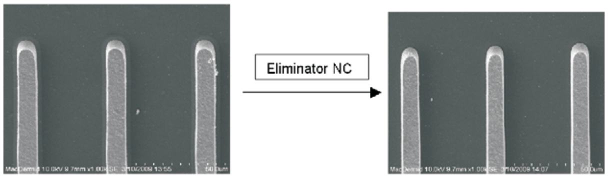

Figure 10. SEM on copper circuit trace before and after the process

Filter Fit Correction Method: Proza (Phi-Rho-Z) Element Line	Int. Cps/nA	Int. Error	Element Wt.%	Filter Fit Correction Method: Proza (Phi-Rho-Z) Element Line	Int. Cps/Na	Error	Element Wt.%
C K	72.22	3.44	44.21	C K	93.16	4.01	44.73
N K	3.04	0.74	9.16	N K	4.22	0.84	11.41
O K	21.52	0.77	24.92	O K	25.30	0.81	27.99
Al K	1.05	0.22	0.15	Al K	0.72	0.24	0.09
Si K	1.48	0.24	0.19	Si K	1.00	0.26	0.11
Cr K	4.28	0.63	**1.43**	**Cr K**	0.34	0.28	**0.11**
Ni K	11.12	0.88	**6.71**	**Ni K**	0.47	0.32	**0.25**
Cu K	7.12	0.87	5.34	Cu K	6.47	0.83	4.30
Pd L	7.63	0.59	2.14	Pd L	11.72	1.13	2.96
Au L	2.32	0.46	5.74	Au L	3.63	0.52	8.05
Total			100.00	Total			100.00

Table 1. EDS data before and after Eliminator NC process

EDS indicated both Ni and Cr reduced dramatically, below 0.5%, after Eliminator NC process.

Cross sections were prepared to measure fine line width to check if there was any line loss during the process. The measurements were made at the top, middle and bottom of the copper fine lines.

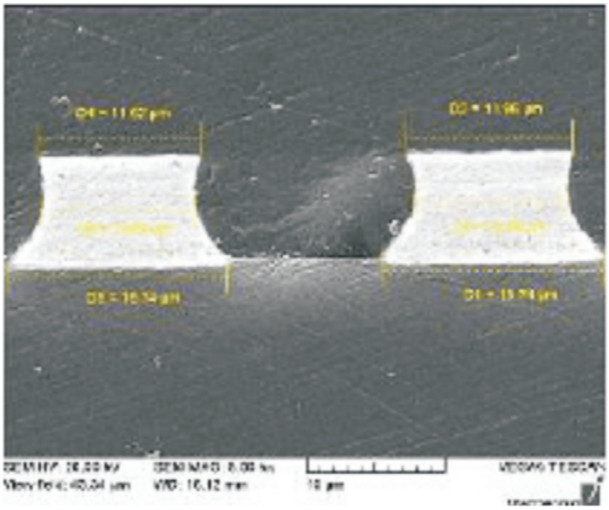

Figure 10. SEM on copper circuit trace cross-section

Lines measured	# 1 (μm)	# 2 (μm)	# 3 (μm)	# 4 (μm)	Average (μm)
Top	11.48	11.57	11.43	11.71	11.55
Middle	10.58	10.72	10.88	11.00	10.79
Bottom	15.58	14.53	15.38	14.39	14.97

Table 2. Copper fine line width before the process

Lines measured	# 1 (μm)	# 2 (μm)	# 3 (μm)	# 4 (μm)	Average (μm)
Top	11.85	11.71	11.86	11.95	11.84
Middle	11.00	10.86	10.73	10.86	10.86
Bottom	15.38	15.24	15.66	15.38	15.42

Table 3. Copper fine line width after being processed by HCl predip and Eliminator NC stripping solution, new make-up

Lines measured	# 1 (μm)	# 2 (μm)	# 3 (μm)	# 4 (μm)	Average (μm)
Top	11.57	11.99	12.13	11.57	11.82
Middle	10.72	10.86	11.00	10.86	10.86
Bottom	14.11	14.25	13.82	14.39	14.14

Table 4. Copper fine line width after being processed by HCl predip and Eliminator NC stripping solution, copper concentration in HCl predip was at 122 ppm

The measurements indicated that the chemistry had almost on attack on copper circuits even the predip had certain amount of copper in it.

Conclusions

The two-step etching process, etching tiecoat after stripping resist, was developed. The Ni/Cr alloy etch chemistry, Eliminator NC, can efficiently remove Ni/Cr alloy without attacking on copper circuit trace with bath temperature at 45 -50 ^{o}C. Ni/Cr removal rate was increased with higher acidity and higher chloride concentration, while the chemistry had wide operation window with accelerator concentration, NC 7582, at 100 ml/L. Predip step, hydrochloric acid, could help reduce the defects caused by excess copper leftover from copper etch process. EDS data showed Ni/Cr residue were all below 0.5% after the boards went through the chemistry, while measurement on fine lines indicated there was almost no reduction on copper fine line circuits.

Acknowledgments

The authors would like to acknowledge the contributions from Analytical Methods Development Group at MacDermid, Inc., we greatly appreciate Mr. Ed Komarnichi's work on SEM and EDS.