

Adhesiveless Copper on Polyimide Substrate with Nickel-Chromium Tiecoat

Bergstresser, T.¹, Hilburn, R.¹, Kaplan, H.², and Le, R.²

Abstract

Adhesiveless copper on polyimide substrates are used extensively for high density, flexible circuit applications. A typical construction includes the polyimide substrate, a thin vacuum deposited metal tiecoat, a copper seedcoat, and an electrodeposited copper layer. One or both sides of the polyimide may be metallized, and very thin copper can be provided in order to facilitate formation of fine-line features. Since metal layers are direct deposited, not laminated, the copper profile and bond treatment typically associated with copper foils are not present between metal and dielectric. Adhesion between metallization and dielectric is achieved by performing plasma pretreatment prior to metallization, and by the selection of a suitable tiecoat metal. Tiecoat metal is especially important to minimize adhesion losses associated with circuit processing and subsequent environmental exposures. In this work, characteristics of copper on polyimide substrates with nickel-chromium tiecoat are investigated. Adhesion, before and after exposure to elevated temperature, pressure cooker conditions, and gold plating, is determined as a function of tiecoat thickness. Additional characteristics, including etching performance and a practical example of using the material to manufacture a high-density circuit, are discussed.

Introduction

Adhesiveless copper on polyimide substrates are commonly used for fine-line and high density electronic interconnection applications. Medical, hard disk drive, and COF applications often require line and space features 2 mil and finer. Adhesiveless materials can facilitate fine feature formation because thin copper is available and because the interface between copper and dielectric is smooth. Both attributes result from the fact that adhesiveless materials are manufactured by direct metallization of fully cured polyimide film.

Adhesion between copper and polyimide is an important consideration because there is no copper profile or nodular bond treatment to promote mechanical interlocking. Good adhesion is achieved for these materials by plasma pretreating the polyimide surface and by applying a thin metal tiecoat between copper and polyimide. Common tiecoat metals include chromium and nickel alloys.

Circuit fabrication can degrade adhesion of copper to polyimide. The process steps involve exposure of the materials to harsh chemical environments. Process chemistries can include organic cleaners, highly acidic or basic aqueous solutions, highly aggressive neutral solutions, and in many cases, combinations of all types at different stages of the process. Gold plating solutions can be particularly severe for

adhesion loss, often involving high pH, aggressive cyanide species, or both. A previous study characterized peel strength loss for adhesiveless materials that were gold electroplated using a neutral potassium gold cyanide bath³. Adhesion loss was reduced significantly by application of a thin chromium tiecoat between copper and polyimide. Nickel alloy tiecoats also reduced adhesion loss, but to a lesser degree.

Elevated temperature and humidity can also degrade adhesion for copper - polyimide substrates without tiecoat and cause fabrication or reliability issues. Previous studies characterized peel strength loss for copper on polyimide films after exposure to elevated temperatures³ and after a so-called pressure cooker test⁴. The pressure cooker test involved exposure of the material to 121 °C, 2 atm pressure, and 100 % relative humidity (RH) for up to 168 hours. Chromium and nickel alloy tiecoats were found to reduce adhesion losses after exposure to elevated temperatures. Chromium again performed most effectively. A chromium tiecoat was also found to increase peel strength retention after pressure cooker exposure using two different polyimide films.

In this work, characteristics of copper on polyimide substrates with nickel-chromium (NiCr) tiecoat are investigated. The effort is intended to complement previous work, which was accomplished on substrates with nickel alloy tiecoats that did not contain chromium. Peel strengths, before and after exposure to elevated temperature, pressure cooker

conditions, and gold plating, are determined as a function of tiecoat thickness. Additional characteristics of the nickel-chromium tiecoat, including etching and a practical example of fabricating a circuit, are also discussed.

Experimental

Single-sided copper on polyimide laminates were made using standard commercial practices. The polyimide base material was 1 mil Kapton⁵-E. The polyimide film was plasma pretreated in an oxygen-containing environment prior to metallization. Tiecoat metal and a copper seedcoat about 2000 Å thick were sputter deposited. Tiecoat layer thickness was varied between 0 Å and 200 Å. Target materials were copper (99.99+ % Cu) and nickel-chromium (79.9+ % Ni, 20.0+ % Cr). Samples with commercial Monel 400 (64.8 % Ni, 32.5 % Cu) and chromium (99.9 % Cr) tiecoats were prepared for comparison. Final copper thickness was built-up to about 0.7 mil by electrodeposition.

Peel strength samples were prepared for testing after thermal and pressure cooker exposure as described previously^{3,4}. The samples had 1/8th inch wide etched traces and were exposed to environmental conditioning without back-side copper or laminate backing material.

Samples were prepared for adhesion testing after gold plating using standard commercial practices. Panels were print and etch processed in cupric chloride to create patterns of 10 interconnected 8 mil wide lines and spaces. Soft gold was electroplated using MetPure 99, a commercial neutral potassium gold cyanide bath from Metalor Technologies USA. The overall process included an acid soak, a nickel plate, and a gold strike prior to gold plating. Nickel thickness and gold thickness were each 30 μinch.

Practical adhesion was determined using the industry standard 90° peel strength test. The equipment was a Series 1130 Instron with a Sintech upgrade running Testwork V3.09 software. A 10 lb load cell and a 2 inch/minute crosshead speed were used. Unless otherwise noted, peel tests were performed on samples with 0.7 mil copper without any additional copper build-up. Peel strength measurements on any given sample were replicated at least three times. In the majority of cases, peel strength results were replicated from multiple samples and/or trials as well. Average values are reported.

Peelback samples were analyzed for failure using a Scanning Electron Microscope (SEM) and X-Ray Photoelectron Spectroscopy. The SEM was a Leo model 1450VP variable pressure scanning electron microscope. The XPS unit was a Physical

Electronics PHI 560 ESCA/SAM System equipped with a double pass CMA. The XPS work was carried out using a Mg x-ray source operating at 15 KV and 300 watts power.

Initial Adhesion

Initial peel strength of substrates with NiCr tiecoat are given in Table 1. Results for no tiecoat, monel, and chromium tiecoats are included for comparison.

Table 1: Initial Peel Strength Results

Tiecoat and Thickness	Peel Strength (lb/in)	
	0.7 mil copper	1.4 mil copper
NiCr (50 Å)	4.6	6.5
NiCr (100 Å)	4.1	6.0
NiCr (200 Å)	4.8	7.0
None	4.0	4.8
Chromium (170 Å)	4.7	6.6
Monel (70 Å)	4.4	5.2

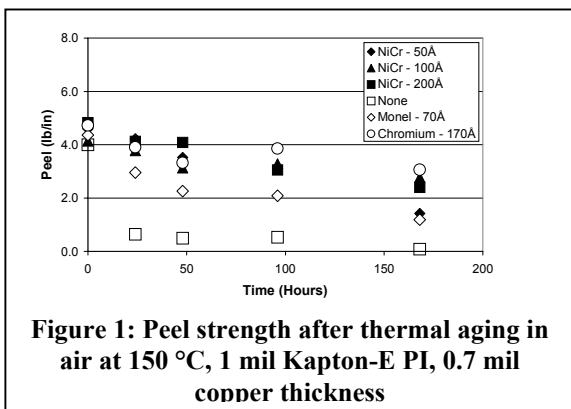
Initial peel strength for all the samples with 0.7 mil copper fall within 4 to 4.8 lb/in. Values are about 1 to 2 lb/in larger for the 1.4 mil copper. All of the values are above the IPC specifications⁶ of 2.0 lb/in for thin materials and 4.0 lb/in for thick materials. The good adhesion arises primarily from the plasma pretreatment. The oxygen containing pretreatment increases oxygen surface concentration⁷, roughens the surface⁸, and may reduce low molecular weight components and volatiles near the surface⁹.

Peel strength reproducibility is about ± 0.5 lb/in. The NiCr and chromium results are comparable for both copper thicknesses. Thickness of NiCr tiecoat does not significantly change initial peel strength. All of the tiecoats appear to provide slight improvement in peel strength compared to the sample without tiecoat. It is unclear whether or not the NiCr provides better initial peel strength compared to monel.

Adhesion After Thermal Aging

Peel strength measurements after thermal aging in air at 150 °C for the different tiecoat constructions are given in Figure 1. Without tiecoat, peel strength declined rapidly with time. After about 24 hours of exposure, only 0.6 lb/in peel strength remained. The rate of peel strength loss increases with temperature. Similar samples without tiecoat lost all adhesion after about 4 hours at 225 °C³.

All of the samples with tiecoat showed improvements in adhesion retention. After 168 hours of exposure, the two thicker NiCr samples had about 2.5 lb/in peel strength. The thinner NiCr tiecoat exposed for the same period of time exhibited about 1 lb/in lower peel strength. Generally, the NiCr tiecoat did not perform quite as well as the chromium tiecoat, but it



performed better than the monel tiecoat. Except for the longest exposure time, little difference was observed between the NiCr samples with different tiecoat thickness. The lower peel strength of the 50 Å sample exposed for 168 hours may be explainable as indicated below.

Metal side and laminate side peelbacks of 50 and 200 Å thick NiCr samples were analyzed by XPS. The samples included those that were exposed to 150 °C for 168 hours and those that were not exposed to any conditioning. Analyses of this nature help to determine peel failure location and the mechanism of peel strength losses.

Both unexposed samples failed within the polyimide, exhibiting primarily carbon, nitrogen and oxygen signals on the trace side peelback surfaces. No tiecoat metals were found. This is consistent with earlier work with other tiecoats³.

Two key features were apparent from the peelback analyses of the thermally aged samples. Both metal-side peelbacks exhibited low percentages (< 3.3 %) of nickel and chromium in addition to carbon, oxygen, and nitrogen. Failure appears to be primarily in the polyimide, but the detection of nickel and chromium suggests localized exposure of the metal interface (pullouts) or thinning of the adhered PI.

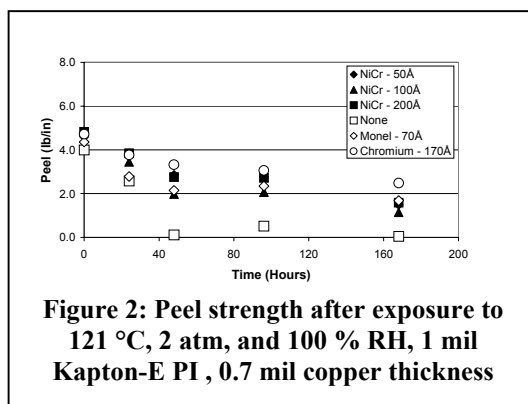
Secondly, copper was found on both the trace side (2.3 %) and polyimide side (0.4 %) peelbacks of the 50 Å NiCr sample. These observations suggest a small amount of copper diffused through the tiecoat into the polyimide. No copper was found on either peelback surface of the 200 Å NiCr exposed sample. This suggests no significant copper diffusion occurred.

Functioning of the NiCr tiecoat during thermal aging is thought to be similar to that suggested in earlier

work for chromium³. The NiCr tiecoat acts as a diffusion barrier for copper. This inhibits significant interface destabilization and prevents the rapid adhesion loss that is observed for materials without tiecoat. Increasing NiCr thickness above 50 Å appears to provide a more effective barrier. Reduced diffusion barrier effectiveness may explain the larger adhesion loss observed for the 50 Å sample exposed for 168 hours.

Adhesion After Pressure Cooker

Peel strength measurements for the different tiecoat constructions after exposure to 121 °C, 2 atm, and 100 % RH are given in Figure 2.



Without tiecoat, peel strength declined rapidly with time. After about 48 hours of exposure, effectively no bond strength remained. All of the tiecoats studied improved peel strength retention significantly. After 168 hours of exposure, the samples with NiCr tiecoat had about 1.5 lb/in peel strength. The samples with chromium tiecoat performed slightly better. They maintained about 2.5 lb/in peels after 168 hours of exposure, which is consistent with earlier studies⁴. It did not appear that NiCr provided added adhesion retention compared to monel. Similarly, it did not appear that increasing NiCr thickness improved performance.

Metal side and laminate side peelbacks of 50 and 200 Å thick NiCr samples exposed to 168 hours in the pressure cooker were analyzed by XPS. No copper or tiecoat metals were detected on the polyimide side surface of either sample. In addition to carbon, oxygen, and nitrogen, only small percentages of nickel were found on the trace side peelbacks. In the case of the 50 Å sample, 2.3 % nickel was found. In the case of the 200 Å sample, 1.4 % nickel was found. The observations suggest failure occurs primarily in the polyimide. There appears to be localized exposure of the metal tiecoat (pullouts), or polyimide thinning, and this suggests interface

weakening. There does not appear to be evidence for copper diffusion through the NiCr.

The NiCr tiecoat is thought to act as a barrier between copper and polyimide. In previous work, degradation of polyimide mechanical properties, perhaps by hydrolysis, was suggested as a possible cause of peel strength losses after exposure to pressure cooker conditions⁴.

Adhesion After Gold Plating

Peel strength measurements after gold plating samples having the different tiecoat constructions are given in Table 2.

Table 2: Peel Strength After Gold Plating

Tiecoat and Thickness	Initial Peel Strength (lb/in)	Final Peel Strength (lb/in)
NiCr (50 Å)	4.44	5.15
NiCr (100 Å)	4.41	4.64
NiCr (200 Å)	4.37	5.37
None	3.46	0
Chromium (170 Å)	4.28	4.49
Monel (70 Å)	3.60	3.23

In each case, 30 μinches of gold were plated on a pattern of 8 mil lines and spaces during a 13 minute time interval.

Referring to the table, the sample without any tiecoat exhibited complete loss of adhesion. A second sample consisting of 1/8th inch wide traces, also without tiecoat, was tested for adhesion loss after gold plating. The second sample exhibited an adhesion loss of 37 %. Gold plating in neutral potassium gold cyanide bath is seen to be highly aggressive environment for adhesion loss.

The NiCr and chromium tiecoats significantly improved the adhesion after gold plating. No loss of peel strength was observed. In fact, the peel strength of these samples actually increased after gold plating. The peel strength increase may be understandable based on the idea that peel strength is a practical measure of adhesion, and the value includes contributions besides intrinsic adhesion^{10,11}. The nickel and gold plating increased the thickness and width of the traces. Also, the different metals and multiple interfaces could require more work to bend than pure copper of equivalent thickness and width. Finally, the increase in peel strength was confirmed with samples consisting of 1/8th inch traces, which also showed increases in peel strength after gold plating.

The sample with monel tiecoat also provided significant improvement in peel strength retention as

compared to samples without tiecoat. However, in the case of monel, a small decrease in peel strength was observed. Hence, the NiCr tiecoat is more effective than monel in reducing peel losses after gold plating. A monel sample consisting of 1/8th inch peel was also tested for peel strength before and after gold plating. In this case, peel strength increased after gold plating, and the increase was comparable to those of the other tiecoat materials.

A peelback of a gold plated sample without tiecoat was analyzed by SEM. For the analysis, one of the 1/8th inch wide traces was peeled back. The resulting SEM photomicrograph is shown in Figure 3. In the figure, region A represents the exposed polyimide surface, while region B represents the interfacial surface of the peeled back metal feature. The very bottom of region B represents the edge of the etched copper trace.

The upper portion of region A shows evidence of disrupted polyimide, indicative of excellent adhesion. The lower portion of region A shows a smooth surface, indicative of little to no adhesion. Similar features are indicated on the underside of the 1/8th inch trace, region B. Failure after gold plating is seen to be an undercut phenomenon. Components of the gold plating bath attack the copper at the polyimide – copper interface. The attack begins at the edge of the trace and progresses inwards with time. In the case of the sample without tiecoat, approximately 200 μm of undercut was observed after about 13 minutes of plating time. Where attack has occurred, there is little to no adhesion. Therefore, with no tiecoat, features with less than 400 μm width would completely delaminate. Features with greater width would remain adhered to the substrate but exhibit loss of peel strength. This is why 8 mil traces

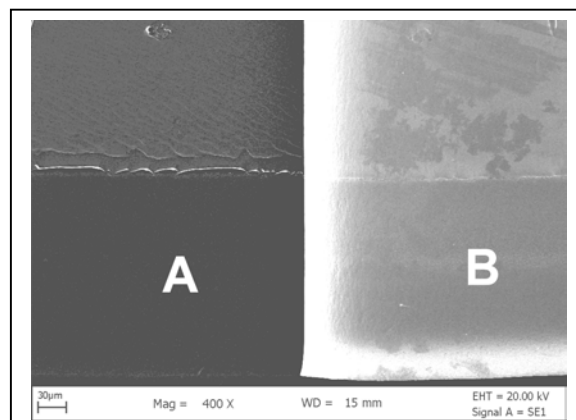
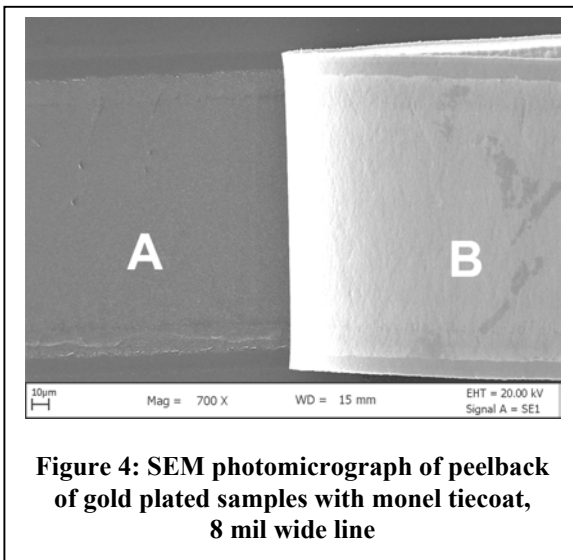


Figure 3: SEM photomicrograph of peelback of gold plated samples without tiecoat, 1/8th inch wide line

delaminated while 1/8th inch traces remained on the board for the non-tiecoat samples.

An SEM photomicrograph of the monel tiecoat sample peelback is shown in Figure 4. The sample had been exposed to gold plating. Again, region *A* represents the exposed polyimide surface, while region *B* represents the interfacial surface of the peeled back metal feature. The SEM photomicrograph confirms that a small amount of undercut, about 10 μm , was observed on the underside of both edges of the trace. This undercut is much less than that observed for the no tiecoat sample and explains the improvement in peel strength retention. It also explains the difference in performance between 8 mil and 1/8th inch peel samples. The 20 μm undercut (10 μm on either side) is 10 % of the 8 mil (200 μm) traces but is insignificant compared to the larger 1/8th inch traces.



SEM was used to analyze peelback surfaces of gold plated 50 \AA NiCr samples. We observed about 3 μm of undercut, which is appreciably less than what was observed for the monel tiecoat sample. The reduced undercut explains the better peel strength retention of the sample with NiCr tiecoat as compared to the sample with monel tiecoat.

Peel loss after gold plating with neutral potassium gold cyanide bath is seen to result from copper undercut at the copper - polyimide interface by components of the plating solution. The NiCr and chromium tiecoats provide protection against the attack. Monel also provides protection, but it is not as effective as NiCr. Fine-line features are more susceptible to adhesion loss from undercut than larger features.

Processing and Application Example

Processing monel and chromium based adhesiveless flexible materials was discussed in an earlier paper¹². General features of processing NiCr based material are the same. As with monel, NiCr can be etched in a single process using cupric chloride. However, the NiCr is slightly less readily etched as compared to monel. Adjusting and maintaining a slightly higher acid level, about 60g/L HCl, is recommended.

Advantages of the NiCr tiecoat were observed in a production environment involving a fine line medical application. The processing was challenging, involving localized high temperatures from a laser microvia fabrication as well as electroplated gold from a neutral potassium gold cyanide bath. Monel tiecoat material had been selected to build the circuit. However, low adhesion and delamination were observed. Improvement was accomplished with process adjustments, but the issue was not eliminated. Switching to the NiCr tiecoat eliminated the adhesion issue and allowed successful fabrication of the part. A key reason the NiCr tiecoat proved successful was the better resistance to adhesion loss after gold plating, as described above.

Summary and Conclusions

Characteristics of copper on polyimide substrates with nickel-chromium tiecoat were investigated. Peel strength after thermal aging, pressure cooker exposure, and exposure to gold plating was measured and compared to results for other tiecoat constructions.

The NiCr tiecoat acts as a barrier between copper and polyimide and reduces adhesion loss after thermal aging as compared to no tiecoat. The NiCr tiecoat is slightly less effective than chromium, but a little more effective than monel. A NiCr thickness greater than 50 \AA may provide some advantage at longer exposure times.

The NiCr tiecoat also reduces peel strength losses after exposure to 121 $^{\circ}\text{C}$, 2 atm, 100 %RH in a pressure cooker. Again, the NiCr tiecoat performs slightly less effectively than the chromium tiecoat. In this case, NiCr and monel performances are comparable, and increasing NiCr tiecoat thickness provides no added benefit.

The NiCr tiecoat significantly improves adhesion retention after plating from neutral potassium gold cyanide bath. Performance was comparable to samples with chromium tiecoat and better than samples with monel tiecoat. Peel loss after gold plating results from copper undercut, at the copper - polyimide interface, by components of the plating

solution. The NiCr tiecoat effectively minimizes the attack. Fine-line features are more susceptible to adhesion loss from undercut than larger features.

The superior performance of NiCr tiecoat in reducing adhesion losses after gold plating and environmental exposure was demonstrated by experience fabricating a fine-line circuit in a production setting. Low adhesion and delamination had been observed on circuits made from laminate with monel tiecoat. Process conditions were challenging, involving elevated temperature and gold plating. Switching to the NiCr tiecoat eliminated the adhesion issue and allowed successful fabrication of the part.

Acknowledgements

The authors acknowledge contributions from James Winchester and Georgia Crosby for adhesion testing, Kathy Prokop for SEM analyses, and Joe Potkonicky for XPS analyses. Other colleagues in R&D at Gould Electronics in Eastlake, Ohio also contributed to this work.

References

1. Gould Electronics Inc., Eastlake, OH
2. Siemens, AIM Facility, Canoga Park, CA
3. Bergstresser, T.R., Bergkessel, N.E., Chiang, S.K., Poutasse, C.A., and Russell, D.B., 'Peel Strength of Adhesiveless Polyimide Laminates after Thermal and Chemical Exposure' in Proceedings of Flexcon, San Jose, CA, October 19-20, 1997.
4. Bergstresser, T.R., Bergkessel, N.E., and Poutasse, C.A., " in Proceedings of the Fifth International Conference on Flexible Circuits, San Jose, CA, September 15-16, 1998.
5. Kapton is a registered trademark of E.I.DuPont de Nemours & Co.
6. IPC-FC-241C/18 in Amendment 1, October 1995.
7. Bergkessel, N., Bergstresser, T., Chiang, S.K., and Russell, D., " in Proceedings of the IPC 3rd Annual Flexible Circuits National Conference, Phoenix, AZ, May 19-20, 1997.
8. Davis, M., Gould Electronics, Internal Report, 2002.
9. Liston, E.M., Martinu, L., and Wertheimer, in Plasma Surface Modification of Polymers, ed. by Strobel, M., Lyons, C., and Mittal, K., pp. 3-39, 1994.
10. Mittal, K., J. Vac. Sci. Technol., Vol. 13, No. 1, p. 19, 1976.
11. Kim, Kyung-Suk and Kim, Junglhl, Trans. ASME, J. Eng. Mater. and Technol., p. 266, July 1988.
12. Bergstresser, T.R. and Sallo, J.S., in Proceedings of the IPC 5th Annual Flexible Circuits National Conference, Denver, CO, June 9-10, 1999.