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Thin Film Corrosion

By M. K. Raut

Published June 1980

Final Report

Prepared for the United States Department of Energy
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Bendix Kansas City Division

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By M. K. Raut

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Final Report
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THIN FILM CORROSION

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Prepared by M. K. Raut

Corrosion of chromium/gold (Cr/Au) thin films during photolithography, prebond etching, and cleaning was evaluated. Vapors of chromium etchant, tantalum nitride etchant, and especially gold etchant were found to corrosively attack chromium/gold films. A palladium metal barrier between the gold and chromium layers was found to reduce the corrosion from gold etchant.

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SUMMARY

The purpose of this project was to investigate sources and controls of thin film corrosion caused by photolithography prebond etching and cleaning. This work was motivated by the high reject rate of thin film networks (TFNs). The high reject rate was the result of metallization adhesion failures in lead frame bond pull tests.

Chromium/gold (Cr/Au) thin films were exposed to vapors of various solutions (etchants, strippers, developers, etc.) used during photolithography prebond etching and cleaning. The films were evaluated with visual examinations and lead frame bond pull tests. Gold, chromium, and tantalum etchants were found to be the main corrosives. Stabilized Cr/Au films had higher corrosion rates than the unstabilized ones.

Because the studies showed gold etchant is highly corrosive to Cr/Au films, the gold etchant diffusion rate through the dry film photoresist was measured. The results indicated that the diffusion rate was slow enough to ensure that the gold etchant does not attack the gold layer beneath the dry film photoresist between the process of gold etching and photoresist stripping. The gold etchant diffusion, however, was monitored visually; a more sensitive method might indicate a faster penetration time.

To minimize any corrosion from prebond ceric ammonium nitrate (CAN) etching, shortened CAN etch time (10 seconds) and prerinse of 10 percent nitric acid was compared to the current 1 minute of CAN etching. The 10-second CAN etch was effective in removing chromium oxide as well as in minimizing the cerium residue at the gold surface.

The effectiveness of dilute CAN etchant as a prebond etch was further studied. When the CAN etchant is diluted to half strength, the etch rate of the stabilized chromium decreases from 30 to 20 Å per second. The slower rate would give more control over prebond CAN etching and, therefore, minimize corrosion caused by leftover cerium residues on the gold layers.

Potentiodynamics (current versus potential) scans were recorded for gold, palladium, and chromium in 1,000 ppm gold etch solution, and their corrosion rates were calculated. The potential differences among the gold-chromium, chromium-palladium, and gold-palladium were measured in this solution; they were 1.15, 1.10, and 0.04 V, respectively. The measurements indicated that placing palladium between the gold/chromium layers will decrease corrosion in TFNs caused by gold etchant.

DISCUSSION

SCOPE AND PURPOSE

This project was begun to investigate sources and controls of thin film corrosion caused by photolithography, stabilization, prebond etching, and prebond cleaning during the fabrication of hybrid microcircuits.

PRIOR WORK

Thin film networks (TFNs) have periodically experienced a high reject rate because of thin film metallization adhesion failures in lead frame bond pull tests. The adhesion failures were thought to be related to highly corrosive chemicals used during photolithography and prebond etching.

Studies by R. Hampy[1] indicated that exposure to gold and ceric ammonium nitrate (CAN) prebond etch vapors causes corrosion in the tantalum-nitride/chromium/gold (Ta_2N/Cr/Au) metallization system.

ACTIVITY

Corrosion Tests With Chemicals Used in Thin Film Processes

To determine which chemicals are most corrosive, Ta_2N/Cr/Au thin films on ceramic and glass substrates were exposed to the common photolithography and prebond etch chemicals. The ceramic substrates were given lead frame bond pull tests. The glass substrates were visually inspected from the back side to look at the chromium layer. Glass substrates with thin film were then subjected to adhesion tape pull testing to qualitatively determine the metallization adhesion.

Four unpatterned samples of Cr/Au, two on glass substrates and two on ceramic substrates, were exposed to gold etch (KI + I_2) vapors. After one film on each type of substrate was stabilized, the films were exposed to the gold etch vapor for 24 hours. Following this exposure, the ceramic substrates showed gross peeling of the gold from the chromium. The metal came off in a large sheet and did not require a tape test or abrasion to start the peeling. A wet spot on the substrate quickly evaporated after the gold was removed.

On the stabilized Cr/Au films on glass substrates, a characteristic labyrinth pattern could be seen from the back side in the chromium layer. This pattern is a small island structure of

chromium surrounded by chromium depletion areas that resulted from stabilization. Following 24 hours of exposure to the gold etch vapors, small stain spots (Figure 1) could be seen from the back side of the glass forming in the chromium layer. These vapor stain spots represent areas where the gold etch vapor penetrated through the gold to the chromium. These small exposure spots could not be seen on the back side of the unstabilized glass substrates.

A tape test on the glass substrate showed chromium and gold peeling from the substrate, leaving small round chromium spots on the glass (Figure 2). These spots were seen on both stabilized and unstabilized substrates where the etch vapors had penetrated and caused an adhesion failure between the gold and chromium layers. The penetration spots were larger on the stabilized sample than on the unstabilized sample. Also, the etchant had penetrated at the edges of the thin film.

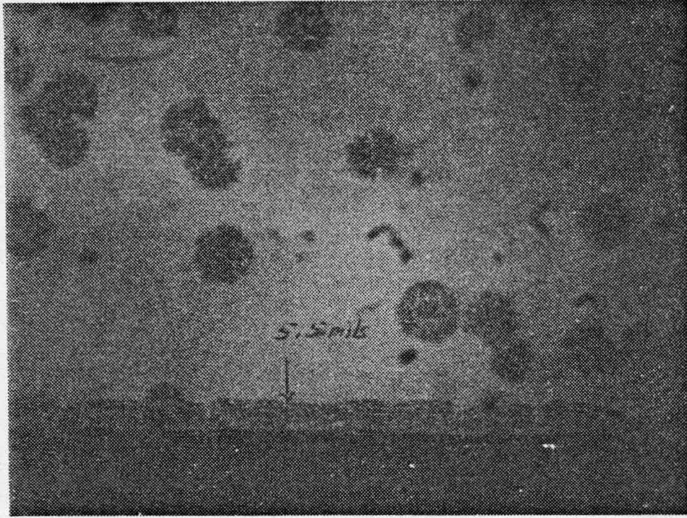
Cr/Au films on two glass and two ceramic substrates were exposed to CAN etch vapors. One film on each type of substrate was stabilized. After 48 hours of exposure to the chromium etch vapors, vapor penetration spots were sighted. Glass substrates were tape tested, and both chromium and gold layers peeled from the glass. A lead frame pull test performed on the ceramic substrates showed an average pull strength of 4.18 N. Of 19 leads pull tested to destruction, 18 were bond delaminations and one was ceramic pullout.

Cr/Au films on glass substrates that were exposed to tantalum etch vapors for 24 hours showed severe etching on the back side of the glass, making it impossible to see the chromium surface from the back side. The films on ceramic substrates were grossly delaminated and left a bare substrate. The tantalum etch vapors apparently penetrated the Cr/Au and attacked the tantalum nitride on the substrate, leaving the chromium and gold to peel. The gold on the glass substrates formed liquid bubbles.

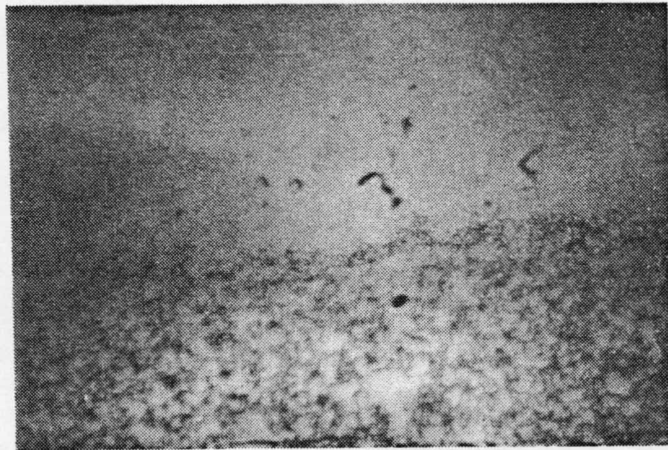
Another group of substrates was exposed for 48 hours to the dry film developer (a proprietary mixture of organic liquid and mildly alkaline buffer solution). No change could be noted on stabilized and unstabilized glass substrates. The lead frame pull strength on the surrounding substrate showed an average of 5.07 N with 18 bond delaminations and one ceramic pullout.

Several Cr/Au film substrates were exposed for 48 hours to dry film stripper (3 parts methylene chloride to 1 part methyl alcohol) vapors. The glass substrates were neither penetrated nor damaged. During the lead frame bond test on ceramic substrates, the substrate was broken.

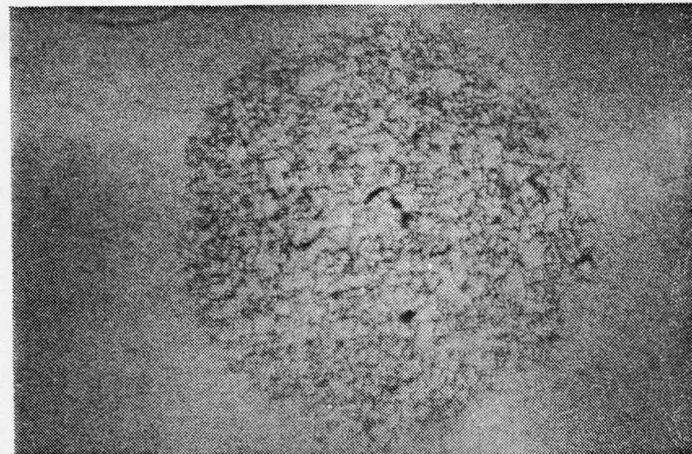
Glass substrates showed no change after several Cr/Au films were exposed for 48 hours to the AZ developer (approximately 0.5 N



PENETRATION THROUGH BULK GOLD (ROUND SPOTS) AND EDGE (STRIPE)

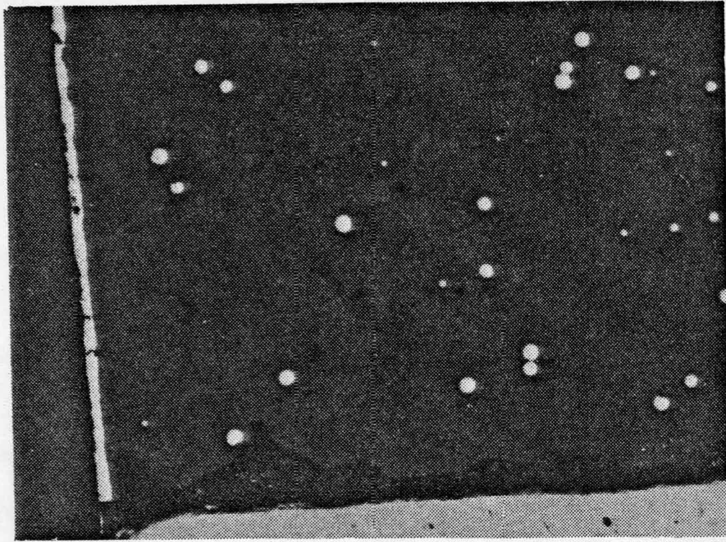


PENETRATION (APPROXIMATELY 125 μm FROM EDGE OF SAMPLE.) LINES ARE WHERE CHROMIUM HAS DIFFUSED INTO GOLD



PENETRATION THROUGH BULK GOLD INTO CHROMIUM (SPOT SIZE APPROXIMATELY 200 μm)

Figure 1. Back Side of Cr/Au Glass Substrate After 24 Hours Exposure to Gold Etch Vapors



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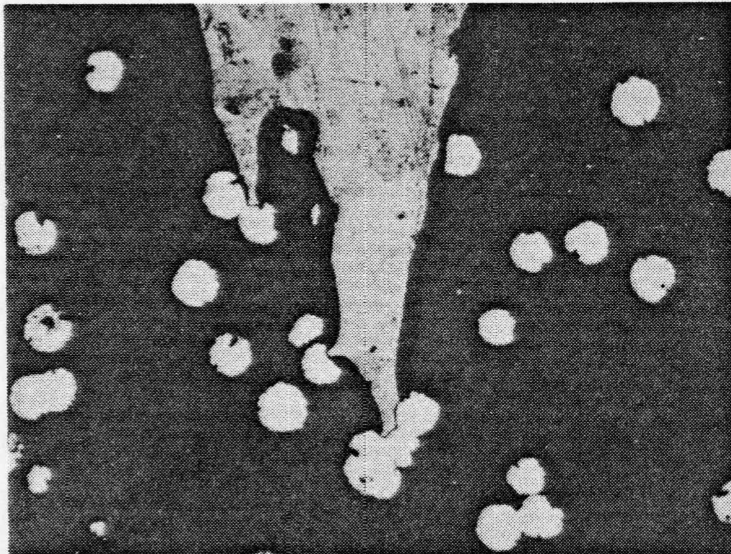
ISLANDS OF CHROMIUM WHERE PENETRATION OCCURRED ON UNSTABILIZED SUBSTRATE



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ISLANDS OF CHROMIUM WHERE PENETRATION OCCURRED ON STABILIZED SUBSTRATE

Figure 2. Tape Test of Cr/Au Substrate After 24 Hours Exposure to Gold Etch Vapors

alkaline-based wet film developer) vapors. Lead frame pull tests on the ceramic substrates showed an average of 12.54 N and all heel failures.

On Cr/Au films that were exposed for 44 hours to the vapors from a sodium-hydroxide-based dry photoresist stripper, there was no evidence of degradation. The ceramic substrate was broken during the lead frame bond test.

Films exposed to trichloroethylene vapors showed no evidence of degradation. The lead frame tested on the ceramic substrates averaged 6.94 N with 14 bond delaminations and 5 heel failures.

Substrates exposed to isopropyl alcohol for 44 hours showed no degradation. The lead frame pull tests averaged 7.65 N with 13 bond delaminations and 6 heel failures.

Films exposed to deionized water vapors for 43 hours showed no film degradation on the glass substrates. Lead frame pull tests averaged 2.62 N with 100 percent bond delaminations.

Four Cr/Au substrates were coated with dry and wet photoresist. After 49 hours, the glass substrates showed no chromium or gold degradations.

Two stabilized and two unstabilized substrates were exposed to cyanide etch vapors. After 7 days, there was no evidence that the cyanide vapors had penetrated the Cr/Au layers. A tape test and abrasive test did not remove the gold or the chromium from the glass substrate.

A Cr/Au glass substrate with an exposed and developed photoresist pattern was placed in the gold etch vapor environment. After 24 hours, the stabilized, dry film sample showed vapor penetration into the Cr/Au. Areas that were resist covered did not differ from areas that were not. A tape test made after 48 hours showed that gold had peeled from the substrates, leaving a large number of chromium spots and a uniform chromium pattern along the edge of the substrate where the gold etch vapors had penetrated.

The stabilized, wet film resist substrate that was exposed to the gold etch vapors showed penetration where the wet film was not on the surface. But where the wet film was protecting the gold, very little penetration through the photoresist was noted. Following 48 hours of exposure, a tape test peeled the gold from the chromium, leaving small chromium circles in the unprotected areas.

Dry film photoresist on unstabilized substrates showed no penetration after 24 hours of exposure to gold etch vapors. After 48 hours, the dry film photoresist offered little protection to the surface, because the photoresist was penetrated. A tape test peeled the gold from the chromium, leaving smaller and fewer chromium islands than those on the stabilized sample.

After 48 hours, the wet film sample that was not stabilized showed slight penetration on the back side of the glass. Tape tests revealed small chromium circles on the areas that were not protected with a wet film resist.

A glass substrate with a Cr/Au pattern was etched before being exposed to gold etch vapors. Two samples were prepared. One was patterned with dry film resist and the other was patterned with wet film resist before etching. Also, substrates were stabilized and unstabilized for each sample. Photoresist was removed before gold exposure.

The stabilized, dry photoresist sample showed uniform penetration following 24 and 48 hours of exposure to the gold etch vapors. (Figures 3 and 4 show these results on a 1270-μm conductor.) Wet film stabilized samples showed about the same amount of penetration after 24 and 48 hours.

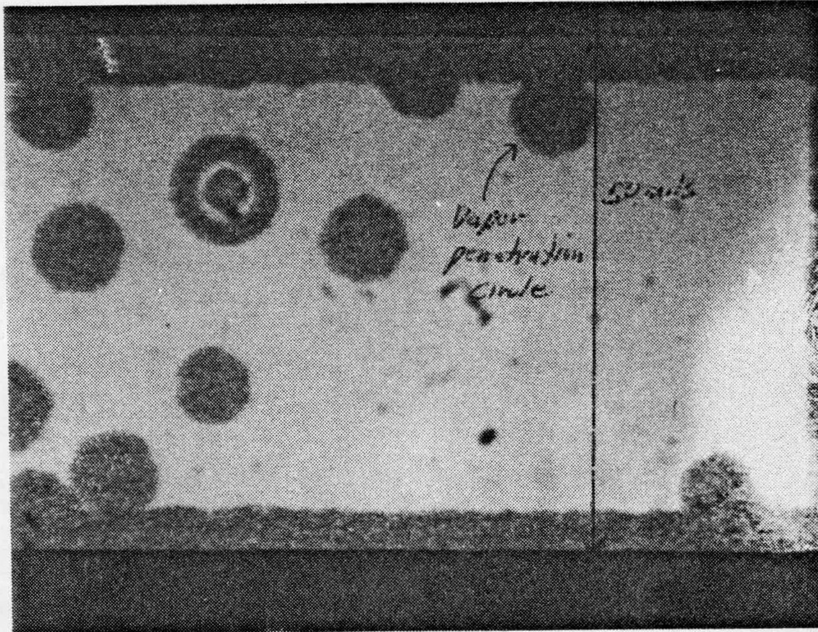
The dry film sample which was not stabilized showed very slight penetration following 48 hours. After the same time, the wet film unstabilized sample also showed a slight penetration. Following 48 hours of exposure to the vapors, the unstabilized dry and wet film samples were stabilized for 2 hours at 300°C. This stabilization made vapor penetration spots more visible from the back side of the glass.

A sample with a Ta_2N/Cr/Au film on a glass substrate was exposed to gold etch vapors. One sample was stabilized and one was not. On both stabilized and unstabilized samples, no penetrations could be seen from the back side of the glass because the Ta_2N layer interfered with inspection. A tape test peeled the gold from the ceramic. There were no visible chromium islands on this sample, although they may have blended in with the Ta_2N layer remaining on the substrate.

Glass substrates (95 by 114 mm) with chromium and electroplated gold, one stabilized and one unstabilized, were exposed to gold etch vapors for 27 hours. The stabilized sample showed a very slight penetration of the gold etch vapors from the back side. After 195 hours, a few penetration spots were seen, though fewer than in similarly treated evaporated samples.

The sample that was not stabilized but was exposed to gold etch vapors did not show any penetration spots. A tape test showed that the gold would peel, leaving small chromium circles (about one spot per square centimeter) similar to circles previously seen. Besides small chromium spots, the uniform chromium line around the edge of the sample indicated that the vapor also had worked in from the edge on the gold-plated samples.

Substrates with phased Cr/Au from a production evaporation system were exposed to gold etch vapors. Both the stabilized and the unstabilized samples showed many penetration spots after 1 to 4 hours. Vapor penetration spots from the unstabilized film were almost as visible as those from the stabilized film. This finding is unusual; most unstabilized film penetration is very difficult to see.



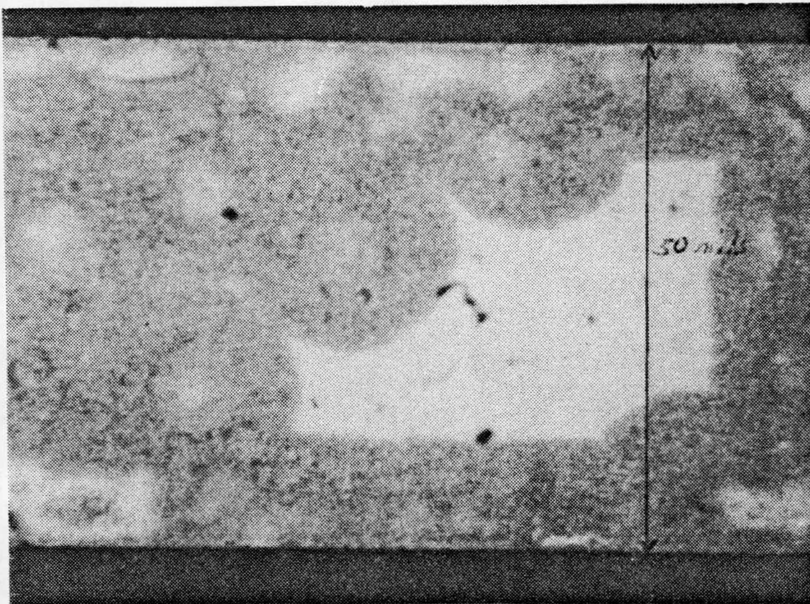
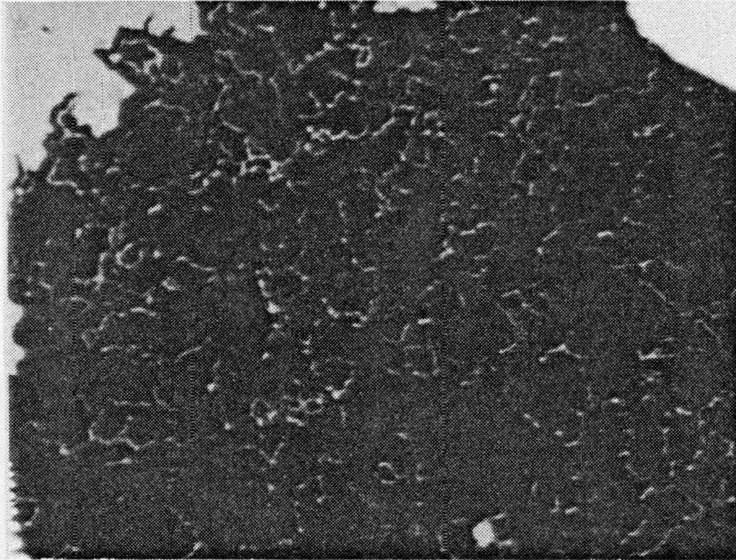
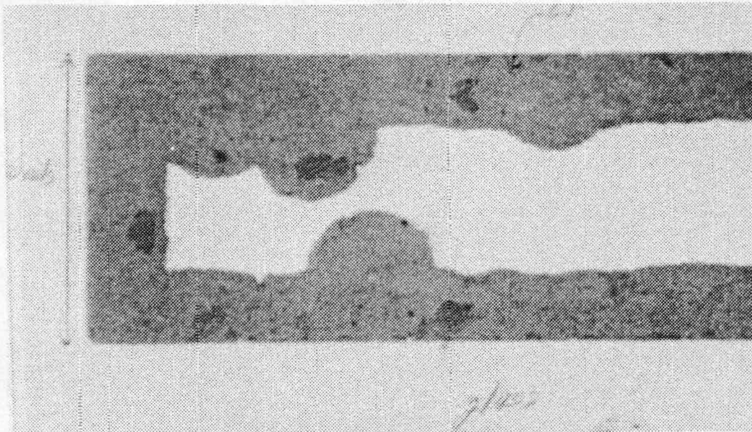


Figure 3. Stabilized Dry Film Sample on a 1270-μm Conductor After 24 Hours (Top) and 48 Hours (Bottom) Exposure to Gold Etch Vapors



REMAINING CHROMIUM ISLAND AFTER TAPE TEST, LINES SHOW CHROMIUM DIFFUSION INTO GOLD

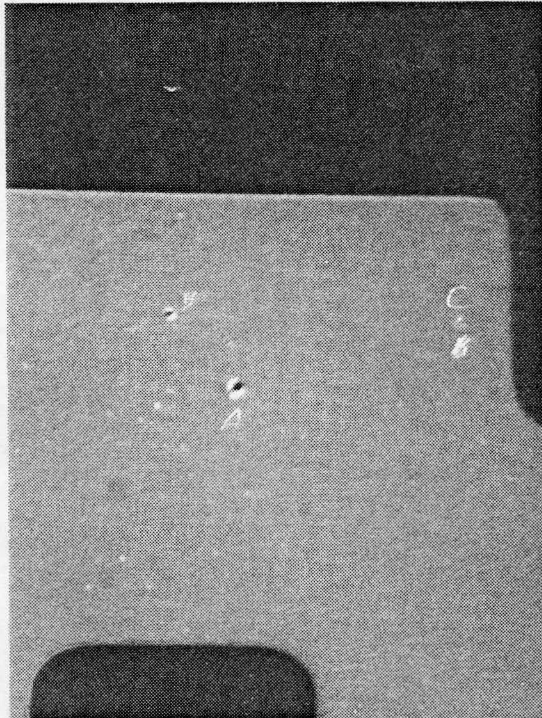


A 1270 - μm CONDUCTOR AFTER TAPE TEST

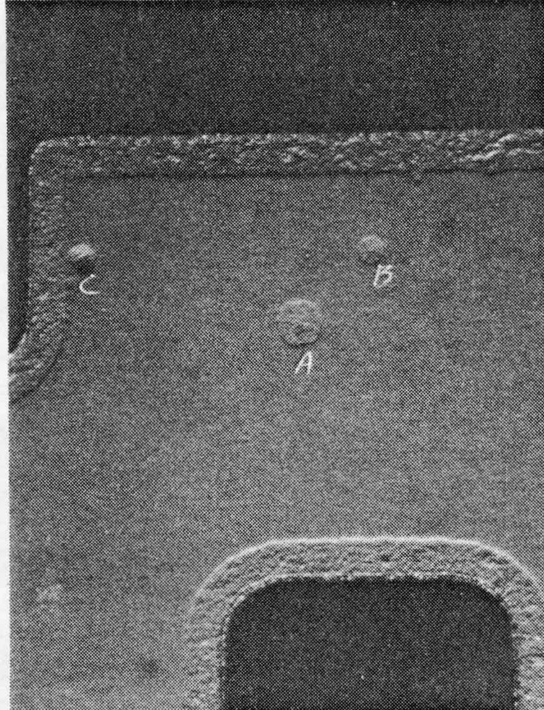
Figure 4. Stabilized Wet Film Sample on a 1270-μm Conductor After 24 Hours Exposure to Gold Etch Vapors

A photopatterned sample with Cr/Au run was etched and then exposed to gold etch vapors. Following 1.5 hours of exposure, many penetration spots were visible. These penetration circles on the back side of the film correspond to gold comets on the front side (Figure 5).

From these above tests, it was concluded that tantalum etch, CAN etch, and gold etch were the worst corrosives for Cr/Au thin films. Corrosives attacked stabilized Cr/Au samples more than unstabilized Cr/Au samples. Liquid photoresist offered better protection against the corrosive vapors than did dry film photoresist.



FRONT SIDE 1.5 HOURS KI AND I_2



BACK SIDE 1.5 HOURS KI AND I_2

Figure 5. Front and Back Side Views of Cr/Au Glass Substrate Showing Penetration Sites and Comets

Penetration of Gold Etchant Through Dry Film Photoresist

Some gold etchant is absorbed by the dry photoresist during gold etching. There was concern that the absorbed gold etchant would penetrate the photoresist and attack the Cr/Au thin film during gold and chromium etching and rinsing.

An experiment was conducted to measure the time the gold etchant took to pass through the photoresist and attack the Cr/Au film underneath. A 6-μm layer of gold was deposited on a glass substrate. A drop of gold etchant was placed on the gold layer of a quarter of the 95- by 114-mm substrate and then observed from the back side. The drop took 20 minutes to pass through the gold layer.

Two quarter sections from the same substrate were then laminated with a dry film photoresist, which was exposed and developed. Overnight, one quarter was exposed to 100 percent RH and the other to less than 30 percent RH. Then, a drop of gold etchant was placed on each of the quarters and the layer was observed

through the back side of the glass. The drop took 2 hours to pass through both the photoresist and the gold layer of the quarter that was left in less than 30 percent humidity, and 40 minutes for the quarter that was left in 100 percent humidity. The tests showed the gold etchant takes approximately 100 minutes to pass through a dry photoresist when a substrate is exposed to 30 percent humidity, and only 20 minutes when it is exposed to 100 percent humidity.

Since this experiment, the interval between gold etching and photoresist stripping has been reduced from 24 minutes to 7, which does not give the gold etchant enough time to penetrate the photoresist and attack the thin film metallization. The gold etchant, however, was detected visually; a more sensitive detection method might reveal a shorter penetration time.

CAN Etching and Rinsing Evaluations

After photolithography, TFNs are baked for 2 hours in a 300°C oven to stabilize the Ta_2N resistors. During this stabilization, chromium diffuses through the gold and chromium oxide forms on the surface. The chromium oxide must be removed before thermocompression bonding. A CAN etch is used for the prebond etch to remove the chromium oxide, which must be removed quickly and completely so that the chromium adhesive layer beneath the gold does not corrode. The current prebond CAN etch process was examined to see if the etching and rinsing could be improved to reduce the likelihood of metallization failures caused by prebond etching.

Several approaches were considered:

- Finding another less corrosive etchant to remove chromium oxide from the TFN surface;
- Decreasing the concentration of the CAN etchant;
- Decreasing CAN etching time; and
- Improving CAN etch rinse removal.

Other known chromium oxide etchants (alkaline potassium permanganate solution, concentrated hydrochloric-hydrazine solution, and alkaline ferricyanide etchant) do not appear to be less corrosive than the currently used CAN etch solution. Therefore, this work was focused on reducing both CAN etching time and CAN etchant concentration, and on improving CAN etch rinse removal.

Seven TFNs from the same 95- by 114-mm substrate were stabilized, CAN etched for various times (60, 55, 40, 30, 20, and 10 seconds), rinsed for 60 seconds with flowing deionized (DI) water, and

dried. The samples were analyzed qualitatively by Auger analysis for chromium and cerium. The analysis indicated that 40 seconds of etching was enough to remove all the chromium from the surface of the TFNs.

Because the main corrosives from the CAN etching process--cerium and chromium--are readily soluble in nitric acid, which is also used in CAN etchant, 10 percent nitric acid was evaluated as a prerinse solution. To test its effectiveness, five TFNs from one 95- by 114-mm substrate were stabilized, CAN etched for 60 seconds, prerinsed for 10, 20, 30, 40, and 50 seconds, rinsed with flowing DI water for 60 seconds, and then dried. The Auger analysis showed that a 10-second prerinse removes all the cerium from the TFN surface.

To find the minimum CAN etching time needed to remove the chromium oxide from TFNs, five TFNs from the same substrate were stabilized and then CAN etched for time periods ranging from 10 to 50 seconds. All the TFNs were prerinsed in 10 percent nitric acid for 10 seconds, rinsed in flowing DI water for 60 seconds, and dried. The Auger analysis indicated that only a 10-second CAN etch plus a 10-second prerinse in 10 percent nitric acid were needed to remove all the chromium oxide from the surface of TFNs.

This CAN etching process was compared to the current process. Four TFNs from a 95- by 114-mm substrate were stabilized and processed by the current prebond CAN etching method that takes 1 minute. Four TFNs from the same substrate were stabilized and processed with a 10-second CAN etch followed by a 10 percent nitric acid prerinse. All of the samples were thermocompression cleaned and bonded with 1270-μm gold-plated lead frames which were then pull tested (Figure 6). Lead frame bond pull test results are shown in Figure 7.

The results show little difference between the bond strengths and the failure modes of both samples. Auger analysis of similarly treated samples indicated that the TFNs that were CAN etched for 10 seconds and prerinsed had no chromium or cerium left on the substrates. The 1-minute etch sample consistently showed cerium on the surface. Therefore, chromium can be removed from the surface of TFNs with 10 seconds of CAN etch. The reduced CAN etching time is also helpful in minimizing cerium residue on the substrate.

Studies also were made to investigate the effectiveness of a diluted CAN etchant in etching stabilized and unstabilized chromium (Figure 8). Stabilized chromium was thought to be harder to dissolve. All the samples in this study had a 250 Å chromium layer. The solutions and chromium etch rates are tabulated in Tables 1 and 2.

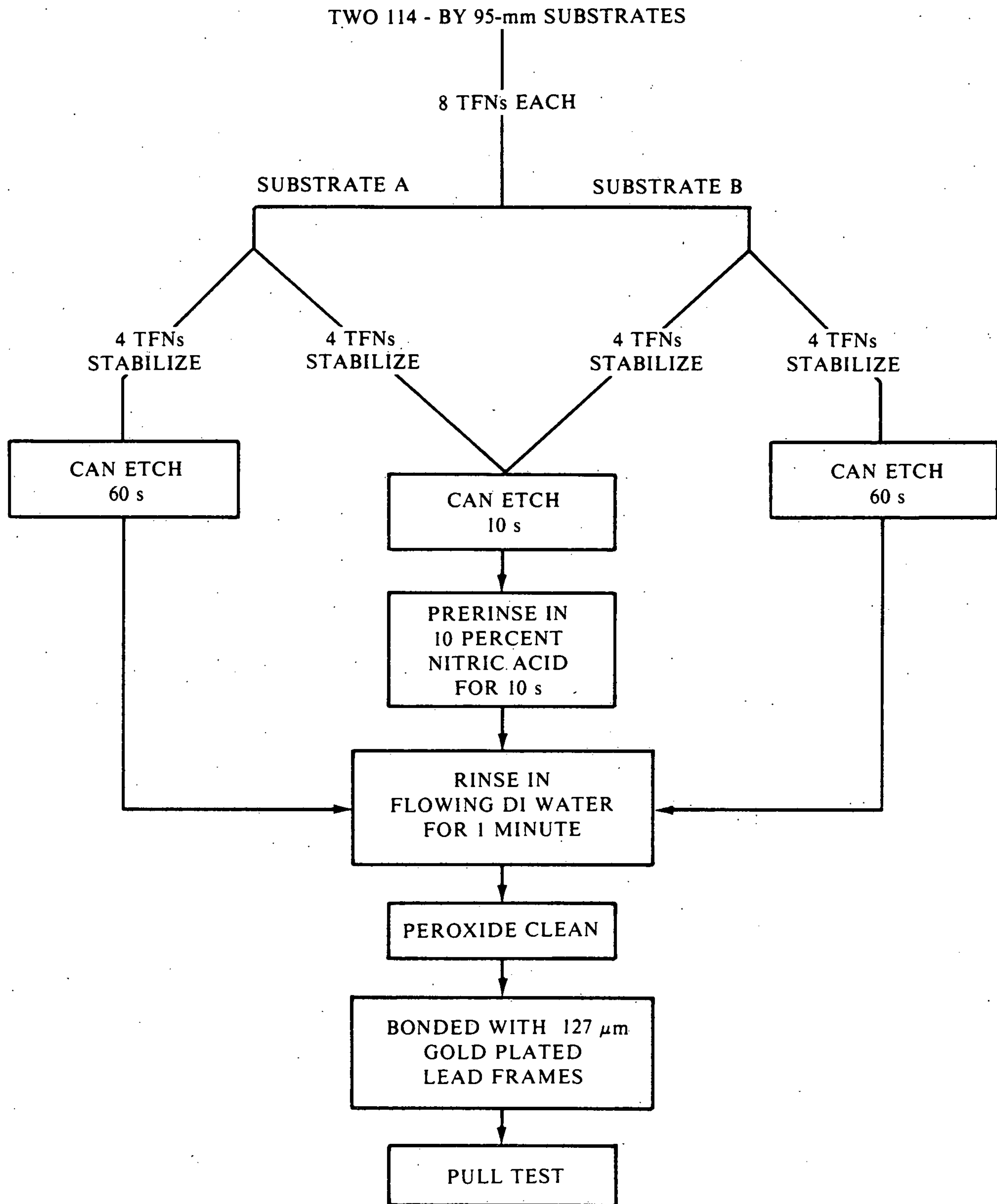
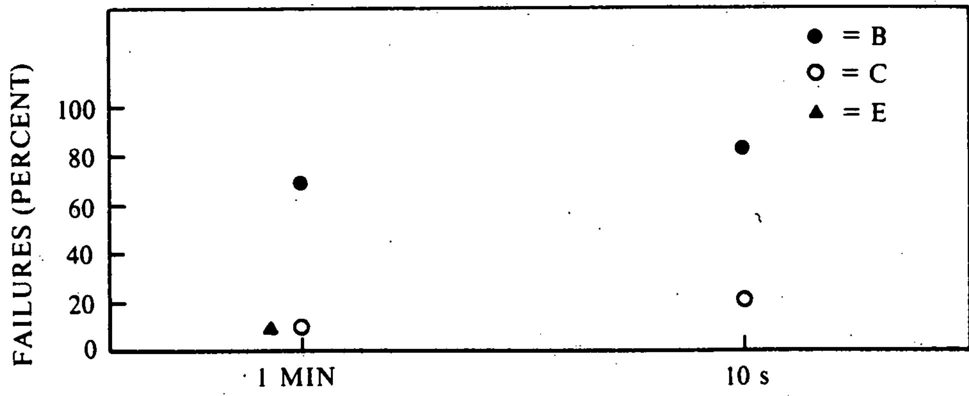
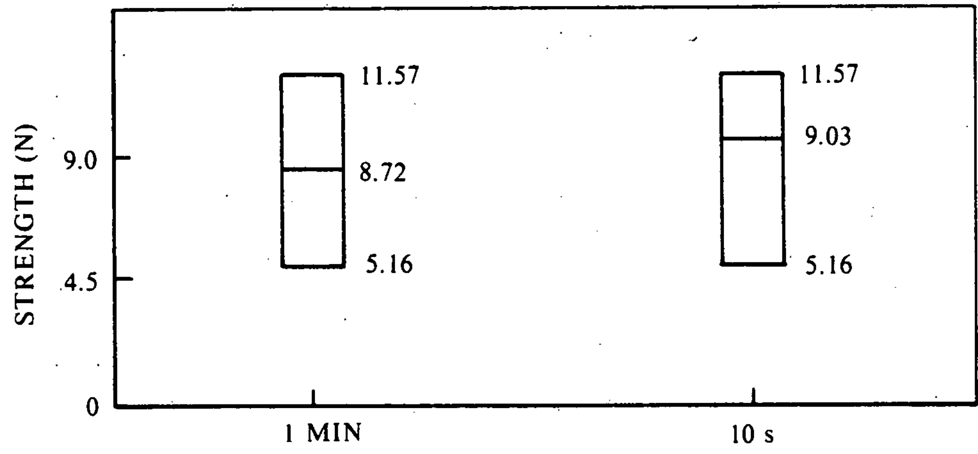


Figure 6. Process Sequence for the CAN Etch Evaluation



a. FAILURE MODES



b. BOND STRENGTH

Figure 7. Bonding Test Results on 1 Minute Versus 10 Second CAN Etched TFNs

The results indicate that stabilized chromium is just as easy to dissolve as unstabilized. Diluted CAN etchant would give more control over the prebond CAN etching process and, therefore, could reduce or eliminate failures caused by the prebond CAN etch process.

Electrochemical Measurements of the Cr/Au System and an Evaluation of Palladium as a Corrosion Barrier

To examine whether a corrosion cell could form between chromium and gold layers when a small amount of gold etchant is left on a substrate in a humid environment, the potential difference

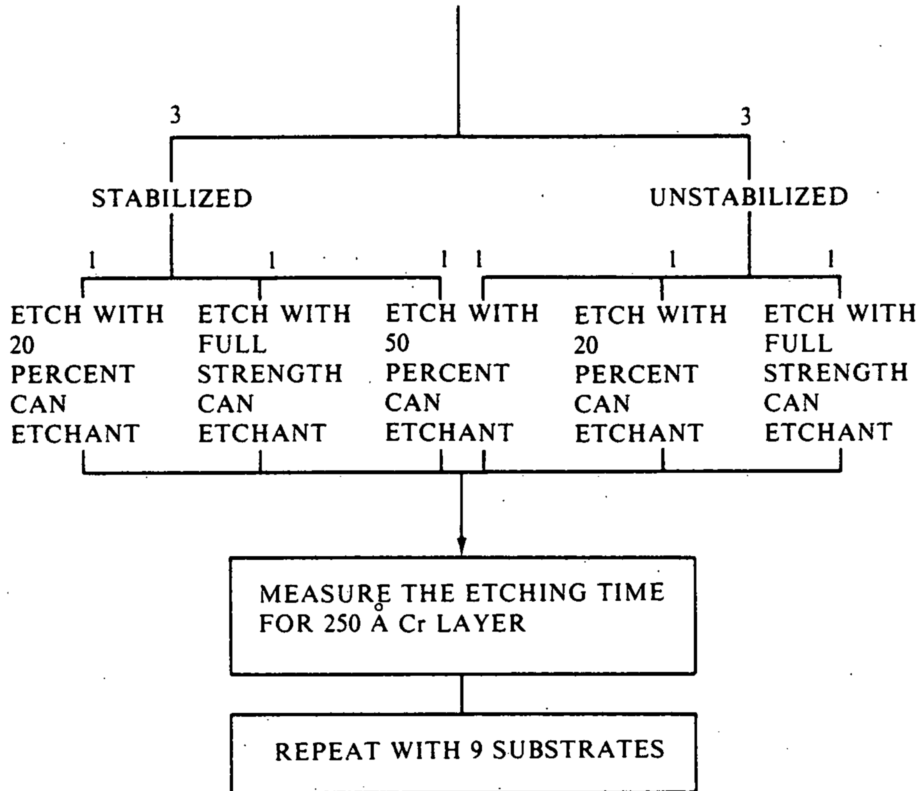


Figure 8. Procedure Used to Compare Etching Time for Stabilized Chromium Layer to Unstabilized Chromium Layer in Various Strengths of CAN Etchants

between chromium and gold metal was measured in a 1000-ppm gold etch solution (1 mL gold etchant diluted to 1 L with DI water). In this solution, chromium acts as a cathode where Cr^{+3} is reduced to chromium, and gold acts as an anode where gold is oxidized to Au^{+3}. The measured potential difference between the two metals was 1.15 V.

This difference indicates that a corrosion cell likely would form between chromium and gold if a small amount of gold etchant is left on the Cr/Au substrate. Forming of the corrosion cell would lead to the gold peeling. The calculated gold corrosion rate in the solution was 4.6×10^{-3} μm per day, or 1.68 μm per year. This is a result of simple corrosion cell formation in which no

Table 1. Chemical Makeup for 1 L of CAN Etchants Used in Chromium Etch Rate Test

Strength of CAN Etchant (Percent)	CAN (g)	HNO_3 (mL)	DI H_2O (mL)
100	164	130	808
50	82	65	904
20	32.8	26	962

Table 2. Chromium Etch Rate in Various Dilutions of CAN Etchant

	Etch Rate (Å/s)	
Strength (Percent)	Stabilized	Unstabilized
100	30	20
50	20	15.8
20	5.9	5.6

current is applied from an external source or supplied to an external circuit. Instead, the current is formed by electrodes of two different metals in metallic contact, which are joined by solutions covering them both with accessibility of oxygen. Such a cell can form when moisture condenses in the pores of a thin film by capillary condensation and when an etchant residue is present on the film.

As soon as gold near the pores is oxidized to Au^{+3}, corrosive material moves horizontally to seek fresh (unoxidized) gold metal. Like most other electrochemical reactions in a cell, this is a surface reaction, and the corrosion penetration spots are noticed only at the Au/Cr interface. The cross section of this corrosion cell is shown in Figure 9.

To prevent formation of this corrosion cell, a palladium layer can be placed between the chromium and gold layer at the corrosion barrier. The potential difference between palladium and

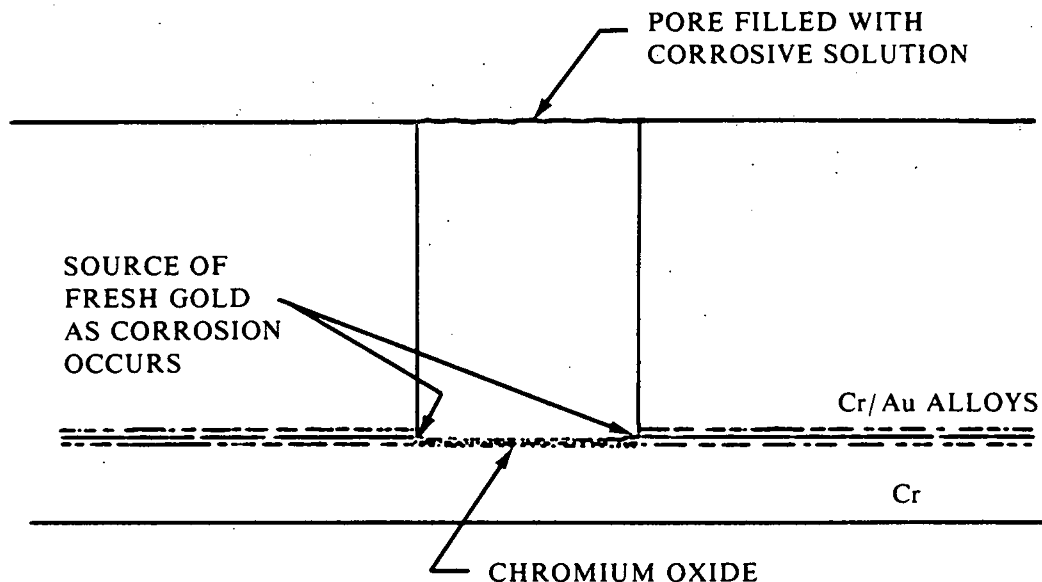


Figure 9. Cross Section of Corrosion Cell Formed at a Cr/Au Interface When Exposed to a Corrosive

gold, as measured in the same 1000-ppm gold etchant solution, was 0.04 V. The potential difference between palladium and chromium was 1.10 V. (Both potential differences are less than the measured potential difference between chromium and gold.) The calculated palladium corrosion rate in this solution (diluted gold etchant) is 2.7×10^{-3} μm per day, or 0.98 μm per year.

These measurements indicate that placing palladium between the Au/Cr layers decreases the chances of a corrosion cell forming between gold and palladium to almost zero. A corrosion cell can be formed between the chromium and palladium layer; however, palladium is less porous than gold, and it is harder for any corrosive material to go through both gold and palladium to cause corrosion between the chromium and palladium layers.

ACCOMPLISHMENTS

Corrosive effects of etchants, photoresists, photoresist developers, and photoresist strippers on thin film Ta_2N/Cr/Au were evaluated. Vapors of gold etchant, chromium etchant, and Ta_2N etchant were found to be corrosive to the films, while the other chemicals used in photolithography and cleaning were not. Gold etchant, which is the most corrosive, attacks the interface between the chromium and gold. Stabilized films were more quickly attacked by gold etchant than were unstabilized films.

By observation, gold etchant was found to diffuse through dry film photoresist in 100 minutes at 30 percent RH and in 20 minutes at 100 percent RH. A decrease in CAN etch time from 1 minute to 10 seconds, and the introduction of a nitric acid prerinse eliminated cerium residue from the surface of stabilized TFNs and still removed the chromium oxide from the surface. Diluted CAN etchant dissolved the chromium layer more slowly than the full strength CAN etchant, thereby lending more control over the prebond CAN etching process. Diluted CAN etchant dissolved both stabilized and unstabilized chromium at the same rate. Electrochemical measurements with Cr/Au and chromium-palladium-gold indicated that a residue from gold etchant can start corrosion between the chromium and gold layer. This corrosion can be greatly reduced when a palladium layer is added between the chromium and gold layer.

FUTURE WORK

The following areas are recommended for additional study:

- Comparing the efficiency of full strength CAN etchant to diluted CAN etchant for use as a prebond chromium etchant;
- Determining the rate at which various concentrations of CAN etchant diffuse the gold layer; and
- Evaluating the combined corrosive effects of humidity, gold etchant, and CAN etchant.

REFERENCE

[1]R. E. Hampy and others, A Comparison of the Ta_2N-Cr-Au and Ta_2N-Cr-Pd-Au Hybrid Metallization Systems -- D.C. Electrical Properties, Resistor Aging, Corrosion Resistance, and Chromium Layer Depletion Studies. UNCLASSIFIED. Albuquerque: Sandia Corporation Report SAND 78-0604, July, 1978.

BDX-613-2435

THIN FILM CORROSION, M. K. Raut, Final, June 1980.

Corrosion of chromium/gold (Cr/Au) thin films during photolithography, prebond etching, and cleaning was evaluated. Vapors of chromium etchant, tantalum nitride etchant, and especially gold etchant were found to corrosively attack chromium/gold films. A palladium metal barrier between the gold and chromium layers was found to reduce the corrosion from gold etchant.

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