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Thin Film Gold Etchant Formulation and Rinse Removal

By M. K. Raut

Published July 1980

Final Report

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

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THIN FILM GOLD ETCHANT FORMULATION
AND RINSE REMOVAL

By M. K. Raut

Published July 1980

Final Report
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THIN FILM GOLD ETCHANT FORMULATION AND RINSE REMOVAL

BDX-613-2393, Final Report, Published July 1980

Prepared by M. K. Raut

The chemistry of gold etchant solutions used in photolithography of thin film networks (TFNs) for hybrid microcircuits was reviewed. The formulation and operating limits were revised to ensure that the initial solution makeup is always within required values for iodine concentration and specific gravity and that the etchant will not be used for an extended period of time. Rinsing procedures for removal of the gold etchant from the TFNs were evaluated. Increasing the rinse time beyond 15 seconds in deionized water does not significantly improve the removal of iodine. Nitrogen bubble burst, increased temperature of the rinse water, methyl alcohol rinse, and potassium iodide solution prerinse were shown to be effective in improving the rinse removal of iodine. Production requirements for stripping time for wet photoresist were shown to be more than three times longer than necessary to ensure that the photoresist was completely removed.

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SUMMARY

The purpose of this project was to establish methods and limits of control for the chemistry of the solutions used in photolithography of thin film networks (TFNs) for hybrid microcircuits and to develop a spray processing capability for manufacturing TFNs. Gold etchant formulation and operating limits, rinse removal of gold etchant, and stripping characteristics of liquid photoresist were evaluated. No work was conducted on spray processing because improved line definition capability for thin film networks was no longer needed.

Thin film production yield problems resulting from metallization adhesion failures, corrosion of resistors, and thermocompression bond delaminations indicated that improved understanding and control of chemical solutions used in photolithography were needed. The formulation and operating limits of the potassium iodide/iodine solution used to etch the gold were evaluated and redefined. Tests were conducted which showed that increasing the concentration of potassium iodide for a fixed concentration of iodine increases the rate of gold etching. The gold etchant formulation was changed so that the initial value of normality of iodine is always 1.0 and the initial specific gravity is 1.250 ± 0.005 . A limit was placed on specific gravity so that the etchant is discarded when the specific gravity increases by 0.020.

The rinsing process used to remove residual gold etchant was evaluated with respect to type of rinsing solution, temperature of rinsing solution, flow rate of rinsing solution, and rinse time. Methyl alcohol was shown to rinse the etchant from the substrates in about 10 seconds compared to 20 seconds for deionized (DI) water. Nitrogen bubble burst, increased temperature of the rinse solution, and potassium iodide solution prerinse were shown to increase the amount of gold etchant removed from the substrate. Rinsing tests with deionized water showed that most of the etchant was removed from the substrate within the first 15 seconds. As a result of these tests, the gold etchant rinse removal steps were changed from a two-step 1-minute/5-minute process to a three-step 5-second/10-second/15-second process in cascaded DI water with nitrogen bubble burst.

The occurrence of carbon residues on TFNs in post-photolithographic processes and bond delaminations in thermocompression bonding of lead frames and beam lead devices prompted an investigation of the process for stripping AZ liquid photoresist from thin film networks. Tests showed that the production stripping times were

three times longer than necessary to ensure that the liquid photoresist was completely removed. However, even when visible amounts of photoresist were purposely left on TFNs, no increase in bond delaminations or decrease in pull strength was observed. It was concluded that photoresist residues did not cause the bond delaminations and carbon residues which occurred in production.

DISCUSSION

SCOPE AND PURPOSE

This project was initiated to establish methods and limits of control for the chemistry of the solutions used in photolithography of TFNs and to develop a spray photoprocessing capability for manufacturing thin film networks (TFNs) for hybrid microcircuits (HMCs). The project was to include conducting tests to determine the controls necessary for photolithography solutions to ensure the quality of TFNs and building and evaluating a prototype spray processor especially designed for TFNs.

PRIOR WORK

Problems encountered in TFN manufacturing indicated that improved understanding and control of solutions used in TFN photolithography were needed. Vapors from the potassium iodide/iodine solution used for gold etching were shown to cause complete delamination of the gold conductive layer from the underlying chromium and tantalum nitride (Ta_2N) layers. A dry film stripper used in some TFN manufacturing caused several TFN lots to be scrapped when the stripper was used at elevated temperature. The stripper attacked the Ta_2N resistor material.

Spray developing of dry film photoresist was determined to be necessary to obtain the conductor line definition required for RF circuits with vias. Although acceptable line definition was being obtained for TFNs using spray developing, immersion etching, and immersion stripping processes, improved line definition was expected to be needed for future TFNs. Moreover, spray etching and rinsing processes were expected to produce less undercutting than immersion processes and to reduce the time of exposure of the TFNs to corrosive etchants. However, commercial spray processing equipment was available only for printed circuit boards much larger than TFNs. A small chamber spray processing system for TFN photolithography was designed and a model chamber was made and evaluated. The spray chamber allows production of dry film line width variations of half the tolerance permitted on RF HMCs.

ACTIVITY

Gold Etchant Limits and Characteristics

Recurring thin film adhesion problems in HMC manufacturing indicated a need for better understanding and control of the chemistry

of the solutions used in photolithography. There are three types of solutions (developers, etchants, and strippers) and two types of resist (wet film and dry film) used during photolithography. Previous studies showed that the gold etchant used in the photolithographic process was one of the highly corrosive solutions which can cause loss of adhesion between the chromium and gold layers. Therefore, the main effort in this work was directed toward etchant formulation and control parameters and to optimize the etchant rinsing process.

The solution used for etching of TFNs consists of iodine (I_2) and potassium iodide (KI) in deionized water. The concentration of I_2 is 1.0 normal and concentration of KI is 1.2 normal. The normality (N) of a solution is defined as the number of equivalent weight of solute per liter of solution. Higher concentrations of I_2 result in faster gold etching rates. A 1 N solution will etch slower than a 2 N solution. The normality of iodine is a measure of the iodine atoms present to remove gold. Since iodine has an equivalent weight of 127, a 1 N solution of iodine will require 127 g/L of solution. The 1 N solution used in TFN manufacturing was determined empirically and results in a reasonable etch time (not too fast to cause overetching).

Since iodine is not soluble in water, potassium iodide must be added to allow iodine to go into and stay in solution. Potassium iodide also helps remove gold-iodine compounds from the substrate surface by complexing its iodide ion with those compounds and dissolving them in the etch solution. Increasing the rate of dissolution of the formed gold iodide in the etchant decreases the gold etch (etchant) time. Therefore, increasing the amount of the potassium iodide decreases the gold etch time. This reduction was shown in experiments performed with gold etch solutions (Figure 1).

The gold etchant solution is monitored by measuring its specific gravity. The specific gravity is the ratio of the mass of the solution to the mass of an equal volume of water at a given temperature. By increasing the quantities of KI, I_2 or dissolved gold in an etchant, the specific gravity will increase. As substrates are etched in this solution, the quantity of gold in solution will retard the etching rate and increase the specific gravity. Therefore, maximum and minimum limits have been placed on the specific gravity.

Prior to this investigation, the photolithography specification imposed three requirements on the initial makeup of gold etchant:

- Normality of iodine of 0.9 to 1.1 N,

Figure 1. Gold Etch Rate Versus Amount of Potassium Iodide in Gold Etch Solution

- Specific gravity of 1.15 to 1.25, and
- Mixing ratio of chemicals of 0.2 g potassium iodide and 0.127 g iodine for each mL of water.

The specific gravity as specified was determined to be incorrect for the mix ratio, and limits were changed to 1.25 ± 0.05 .

With additional investigations, the gold etchant formulation requirements were revised to the following:

- A mixing ratio of chemicals of 200 g potassium iodide and 127 g iodine per liter of the solution with deionized water being used as a solvent;
- The normality of iodine became 0.9 to 1.1 N; and
- The specific gravity became 1.250 ± 0.005 .

With these mixing quantities of potassium iodide and iodine in solution, the initial value of normality of iodine is always 1.0

and the initial specific gravity is within the limits. The solution is discarded when the specific gravity of the solution is increased by 0.020. These limits ensure that the proper ratio of chemicals is used in mixing and that etchant is not used for extended times. Adequate control of the gold etching and photo-processing TFNs is thus provided.

Rinse Removal of Gold Etchant

A study was made to determine the optimum process for rinse removal of gold etchant. Optimum gold etch rinsing should eliminate or minimize any diffusion of the gold etchant through the photoresist by faster and more complete removal of residual etchant. Five parts were evaluated:

- Comparison made of deionized water and methyl alcohol as effective rinsing solvents;
- Effect of temperature on the solubility of gold etchant in deionized water;
- The rate of the rinsing of gold etchant in flowing deionized water;
- Comparison of current rinsing time to five other rinse time combinations with and without nitrogen bubble burst conditions; and
- Feasibility of potassium iodide solution as a prerinse.

The measurement system used to detect iodine in solution in these tests was an iodide ion selective electrode capable of measuring iodide ion concentration to 10 ng/L.

Comparison of Deionized Water and Methyl Alcohol

Although all of the iodine present in the gold etch solution should be present in its soluble form, some of the iodine could stay in the vapor or solid phase. Since it is known that iodine is more soluble in methyl alcohol than deionized water, the effectiveness of deionized water and methyl alcohol as gold etchant rinses were compared. The procedure used for the comparison is shown in the flow chart in Figure 2.

After two minutes of rinsing, both methyl alcohol and deionized water removed the same amount of iodine. However, it took 20 seconds to rinse the maximum amount of iodine off the substrate when deionized water was used, and it took 10 seconds to rinse the maximum amount of iodine off the substrate when methyl alcohol was used. This indicates that the rinsing time can be shortened when methyl alcohol is used to rinse. A major drawback for the

Figure 2. Procedure for Comparing Methyl Alcohol and DI Water as Gold Etch Rinses

use of methyl alcohol is that it strips some of the photoresist. Therefore, it cannot be used before the chromium etching. Methyl alcohol is used in the next step of photoprocessing to strip the photoresist.

Effect of Temperature on the Solubility of Gold Etchant in Deionized Water

The efficiency of rinsing with deionized water with increases in its temperature was measured. The temperature of deionized water in the rinse tank was 11°C on the day the test was conducted. Two TFN substrates (47.5 by 57 mm) with dry photoresist on both sides and a developed pattern on the front side were etched with the gold etchant for four minutes and then rinsed with deionized water at 11 ± 2°C for two minutes. The same experiment was repeated

with the deionized rinsing water at $25 \pm 2^\circ\text{C}$ and at $45 \pm 2^\circ\text{C}$. After each rinsing, the iodine concentration in the rinse water was determined using an iodine/iodide electrode (Figure 3).

This test demonstrates that increasing the temperature of the deionized water increases the efficiency of rinsing the gold etch from the substrate.

Monitoring The Rate of Rinse Removal of Gold Etchant in Flowing Deionized Water

For the third part of the study, the iodide concentration of the rinsing deionized water was measured every 15 seconds. During the rinsing of quarter-sized substrates (47.5 by 57 mm each) with dry photoresist on both sides, the flow of the rinsing deionized water was 2.5 L/minute and its temperature was 15°C . This is the same flow rate that was used in production (Figure 4). Thirty minutes after the rinsing, the rinse water still contained some iodide.

Comparison of Current Rinse Time to Other Rinse Time Combinations With and Without Nitrogen Bubble Burst Conditions

From the previous studies done on the gold etchant rinsing, it was found that most of the etchant was removed from the substrate within the first 15 seconds. This suggested that rinse times could be shortened and still achieve adequate rinsing characteristics. Shortened rinse time has several advantages:

- It shortens the time period for the rinse water containing gold etchant to come into contact with the substrate that is being rinsed;
- It shortens the time substrates are exposed to water;
- It shortens the time period between the etching of gold and the stripping of the photoresist (since dry photoresist was found to be a potential carrier for the gold etchant it would be advantageous to remove the dry photoresist as soon as possible); and
- It reduces the overall photolithography process time.

In this investigation, the present gold etch rinsing time of 1-minute/5-minutes was compared with other rinsing time combinations.

- Substrates laminated with dry film resist on both sides and photoprocessed without a pattern were tested with two-step rinsing without nitrogen bubble burst; Condition 1, Figure 5.

Figure 3. Amount of Gold Etch Rinsed Off the Substrate Versus Temperature of DI Water Rinse

- Substrates laminated on both sides with dry film resist and photoprocessed without a pattern were treated with two-step rinsing with a nitrogen bubble burst; Condition 2, Figure 5.
- Substrates laminated on both sides with dry film resist and photoprocessed without a pattern were tested with three-step rinsing with nitrogen bubble burst applied. The first step was a 5-second rinse; Condition 3, Figure 5.
- Substrates with a photopattern of dry film resist were treated with three-step rinsing (5-second first step) and a nitrogen bubble burst was applied; Condition 4, Figure 6.

Prior studies indicated that the dry film resist absorbs some of the gold etchant. Therefore, for the first three parts of the investigation, no pattern was developed on substrates, allowing the maximum area on the substrates to be covered by a photoresist. Two substrates were rinsed for each rinse condition. Flow diagrams (Figures 5 and 6) show the detailed procedure for each condition. The data obtained in this study is tabulated in Tables 1, 2, and 3 and illustrated in Figure 7.

Figure 4. Concentration of Gold Etch in Deionized Water During Rinsing

The study showed that a nitrogen bubble burst through the rinse tank increased the gold etch rinsing efficiency. When the gold etch was rinsed using a two-step rinse technique without a nitrogen flow, the average amount of gold etch that remained on the substrate was 8.1 μL . When substrates were rinsed using two-step techniques and nitrogen flow, the average amount of gold etchant that was detected was 4.4 μL ; three-step rinsing with a nitrogen flow averaged 4.2 μL . As the total rinsing time is increased, the three-step advantage over the two-step rinse is decreased. After 360 seconds, both samples from the two-step and three-step rinsings had 3.9 μL of gold etchant left. Among the rinsing time combinations that were evaluated, the 5-second/180-second two-step rinsing with nitrogen was found to remove the most gold etchant. After 5 seconds and 180 seconds of rinsing, there was 3.2 μL of gold etchant on the substrate. Increasing the total rinsing time did not significantly improve the efficiency of the gold etch rinse. With the three-step rinsing after the shortest rinse combination (5-second/10-second/15-second), there was 4.1 μL of gold etchant left on the pair of substrates; and after the longest rinse combination (5-second/60-second/300-second), there was 3.8 μL of gold etchant left on a pair of substrates. When substrates were rinsed for 2 hours 55 minutes there was still 3.2 μL of gold etchant left on the substrate.

Figure 5. Gold Etch Rinsing Procedure for Conditions 1, 2, and 3

For the fourth part of the investigation, a 5-second/10-second/15-second rinse was compared to a 5-second/60-second/300-second rinse except that this time the gold etch concentration was monitored after the stripping of the photoresist. At the end of both rinsing combinations there was 0.1 μL of gold etchant detected on the samples. The decrease in the amount of gold etchant left on the substrate is thought to be due to the stripping of photoresist.

Figure 6. Gold Etch Rinsing Procedure for Condition 4

Table 1. Amount of Gold Etch Found on the Substrates and in the Last Stage of Rinse Tank Under Different Rinse Conditions

Rinse Time		Amount of Gold Etch	
Time 1 (Seconds)	Time 2 (Seconds)	Amount 1 ($\mu\text{L/L}$)	Amount 2 ($\mu\text{L/L}$)
Two-Step Rinsing Without a Nitrogen Flow in the Rinser*			
5	15	8.3	8.7
5	30	7.8	9.0
15	15	7.8	7.7
15	30	8.2	8.7
30	60	8.0	6.2
60	300	8.3	4.8
Two-Step Rinsing With a Nitrogen Flow in the Rinser**			
5	15	5.3	10.0
15	30	5.1	9.0
15	60	5.2	8.9
15	180	3.5	8.5
5	180	3.2	8.5
30	60	5.5	8.9
60	300	3.8	8.9
15	10200	3.2	0.2

Time 1 is rinse time in first stage of the rinse tank.

Time 2 is rinse time in the second stage of the rinse tank.

Amount 1 is amount of gold etch left on the substrate after rinsing.

Amount 2 is amount of gold etch found in the last stage of the rinse tank at the end of the rinsing process.

*Condition 1

**Condition 2

Table 2. Amount of Gold Etch
Found on the Substrates
After Three-Step Rinsing
With a Nitrogen Flow in
the Rinser

Rinse Times			Amount of Gold Etch	
1 (Seconds)	2	3	Amount 1 ($\mu\text{L/L}$)	Amount 2 ($\mu\text{L/L}$)
5	10	15	4.1	4.0
5	10	30	4.0	5.1
5	15	30	4.4	5.1
5	15	60	4.3	5.5
5	30	60	4.4	4.7
5	30	300	3.8	3.4

Time 1 is rinse time in first stage of the rinse tank.

Time 2 is rinse time in the second stage of the rinse tank.

Time 3 is the rinse time in the third stage of the rinse tank.

Amount 1 is the gold etch left on the substrate after rinsing.

Amount 2 is the gold etch found on the last stage of the rinse tank at the end of the rinsing process.

Potassium Iodide as a Prerinse

From these studies, it was found that after several different types of rinsing there was still a detectable amount of gold etch present on the substrates. For the further minimizing of the amount of gold etch left on the substrates, substitution of the first deionized water rinsing step with potassium iodide prerinse was investigated. The flow diagram used for this part of the investigation is shown in Figure 8 and the results obtained are shown in Table 4.

Table 3. Amount of Gold Etch
Removed by Hot (40°C) DI
Water After Stripping of
the Photoresist

Rinse Times			Amount of Gold Etch
1	2	3	Amount 1
(Seconds)			($\mu\text{L/L}$)
5	10	15	0.1
5	10	300	0.1

Time 1 is rinse time in first stage of the rinse tank.

Time 2 is rinse time in the second stage of rinse tank.

Time 3 is rinse time in the third stage of rinse tank.

Amount 1 is the amount of gold etch found on the substrate after rinsing.

The results indicate that a 10 second prerinse in 2.0 M potassium iodide solution would improve the gold etch rinsing process.

Stripping Characteristics of AZ Photoresist

An evaluation was conducted to determine the stripping characteristics of AZ liquid photoresist. The purpose was threefold:

- To determine if the current immersion stripping process is adequate to completely remove all resist;
- To determine if residual resist interfered with thermo-compression (TC) bonding; and
- To determine the visual appearance of residual resist as a function of stripping time. The evaluation was conducted using materials and chemicals consistent with the production photolithography stripping processes.

The work was prompted by the occurrence of carbon residues on TFNs in post-photolithographic TFN processes. Additionally,

Table 4. Average Amount of Gold Etch Remaining on the Substrates After Various Prerinse Concentrations and Times

Concentration of KI in Prerinse (M)	KI Prerinse (Seconds)	DI Water Rinse Times (Seconds)*	Gold Found on Rinsed Substrates ($\mu\text{L/L}$)
0.0	0	5/10/15	4.0
1.0	5	60/300	1.0
1.0	5	10/15	1.0
2.0	5	60/350	1.0
2.0	5	10/15	1.0
2.0	10	10/15	0.9

*Refer to Figure 8. First indicated rinse is Time 1, second indicated rinse is Time 2, and third indicated rinse is Time 3.

TC bond delaminations were encountered with both lead frame and beam lead devices. It was desirable to determine if stripping chemicals and techniques were leaving resist residues on the TFN surface which could contribute to bonding problems and to identify what type of indications are present when photoresist is not removed. Visual, Auger, and bonding analyses were used in the evaluation to determine resist removal effectiveness.

Production Stripping of Photoresist

The AZ liquid photoresist is used as the last patterning resist in TFN processing and may, therefore, leave resist residues on the TFN surface. Production stripping techniques require two beakers of stripper solution of approximately 5 L each. The stripper used is Alka Strip 99A mixed in a 1:5 ratio with DI water. Substrates for stripping are immersed and agitated in the first beaker of stripper for 50 to 60 seconds followed by a 50- to 60-second immersion in the second container. Immediately after stripping, substrates are rinsed in a cascade DI water rinse tank (two-stage) for 1 and 5 minutes consecutively. The stripping solution is changed after each day or after stripping 20 large substrates (95 by 114 mm). This process has been used for several years for all types of HMC products with good results.

Figure 8. Flow Diagram for the Potassium Iodide Prerinse Experiment

Test Procedure

The TFNs used for the evaluation were production rejects which had been scrapped for over-high-limit (OHL) resistors. The TFNs were approximately 26 by 26 mm substrates with resistors and conductors predefined by production photolithography. TFNs contained no vias (plated through holes) and conductor patterning was defined from 6 to 7 μm thickness gold.

A block diagram of the test procedure is shown in Figure 9. AZ resist was applied to the substrates after a precleaning. Spin application was used to apply resist to a thickness of approximately 2 μm . The positive resist was not exposed, but TFNs were submerged for nominal times in AZ developer to simulate photoprocessing. After post-baking in an infrared oven, TFNs were submerged in tantalum nitride etchant to simulate resistor etching. Half the TFNs were post-baked before etching in the factory infrared oven and half were post-baked in the laboratory. After etching, parts were rinsed at nominal times in DI water and blown dry with nitrogen. At this point in the processing, the stripping evaluation was conducted.

To simulate production stripping, the experiment was tailored to production quantities of stripper. A ratio, square inches of surface area to quantity of stripper solution, was used as determined by production figures; this was calculated to be 160 mL of solution for the smaller TFNs. This same container of stripper with 160 mL of solution was used in all processing to determine life characteristics.

Initially, a determination was made of actual stripping time by observing when resist was removed from one TFN. Subsequently, this time, T_s , was used as a reference for stripping times; substrates were stripped as a percentage of actual stripping time. TFNs were stripped at times ranging from 200 percent to 50 percent of T_s (Figure 9). Additionally, for a reference condition, one TFN was stripped in two 160 mL beakers of solution at 50 to 60 seconds each, as specified for production substrates. After stripping, TFNs were rinsed in running DI water for 5 minutes, blown dry with nitrogen, and baked for 2 hours at 300°C to simulate the resistor stabilization process. Since all production TFNs receive resistor stabilization, any resist residues found on production TFNs would have been through this process. The reference part was not stabilized.

Visual Inspection for Resist Residue

Most of the strip times resulted in no visible residue at standard microscope magnifications of 10 to 30X. Gross amounts of residue were visible on TFNs stripped at 50 percent of T_s and on TFNs

Figure 9. Procedure for Resist Stripping Evaluation

which were allowed to dry without rinsing. No traces of photoresist were visible on the TFN surface at 70 percent strip time except at the edge, which is characteristic of spinning on resist. Visible residues were left on TFNs stripped at 50 percent T_s and substrates which had been allowed to dry without rinsing. Residue of photoresist has a dark brown appearance and does not cover the surface uniformly. Dark blotches of the resist are apparent at 15 and 25X magnifications. It was possible to see this without magnification, but it was not possible to see photoresist residue on TFNs stripped in excess of 70 percent of the reference time (T_s).

After parts were inspected at standard inspection magnifications, closer inspection was performed at 400 to 500X. This level of magnification showed resist residue at the edges of conductors and on the ceramic surface for all stripping conditions up to and including 100 percent strip time (T_s). These results are shown in Figure 10 at 70 and 90 percent stripping conditions. Resist residues remained adjacent to the conductors until 100 percent strip time. At 100 percent strip time, resist was apparent on the ceramic surface in small selected sites (Figure 10). No residues were apparent on conductors or resistors present at 70 percent or above stripping times; some may be present but are not perceivable on the darker backgrounds. No residues were detectable on the reference substrate stripped in two beakers at production conditions.

A portion of the evaluation was to determine life characteristics of the stripper and to determine actual strip time with relation to specified strip time. The initial strip time (exact strip time was determined by visual conditions) was found to be 27 seconds for TFNs post baked in the factory infrared oven and 21 seconds for those post baked in the laboratory. These times are less than one-third those used for stripping in production application. The exact strip time was remeasured after all strip evaluations were completed. Exact strip times were 25 seconds for production post-bake conditions and 24 seconds for laboratory conditions. Since visual indications of stripping are not completely accurate (approximately ± 15 percent), no significant variations were found between post bake in production or laboratory conditions. Solution life was not being drastically affected by stripping approximately 130 cm² of resist covered TFNs; this is comparable to the 20 substrate limit in production and is considered to be worst case, since the entire TFN was resist coated. These results indicated that both solution life and stripping times used in production were adequate with a large safety factor built into the process.

70 PERCENT OF STRIP TIME

90 PERCENT OF STRIP TIME

100 PERCENT OF STRIP TIME

Figure 10. Residual Photoresist Remaining on TFNs After Various Strip Times (500X)

Bonding Tests

To determine if resist residue interfered with bonding or was a potential contaminant during TC bonding, beam lead devices were bonded and tested for all categories of TFNs stripped. This included TFNs with resist visually apparent. Format 25 devices, which are the most commonly used size at Bendix, were bonded and then destructively pull tested to determine bonding characteristics. Prior to bonding, the TFN samples were prebond cleaned and CAN (cerium ammonium nitrate) etched using factory cleaning facilities and specifications. Since cleaning is part of the procedure prior to bonding, this was done to determine if some resist would be removed by the cleaning operation. After cleaning and TC bonding, Format 25 devices were destructively pull tested; and pull strength and failure mode were monitored, recorded, and compared to TC bond requirements.

The prebond cleaning did not significantly remove any resist residue on the TFNs. This was verified by a visual inspection at both low and high power magnifications. This result was somewhat expected since the resist had been given a stabilization temperature profile as part of the evaluation and was essentially baked onto the surface. TFNs showing resist residues prior to cleaning showed similar amounts of residues afterward. After cleaning, several Format 25 devices were bonded at various locations on each TFN. The parameters used were common to production TC bonding: substrate temperature of 200°C, tool tip temperature of 450°C, and bond force of 450 g. The bonding criteria used for destructively pull testing these Format 25 devices was a 12 g minimum pull strength for each device tested and less than 1 percent "D" failures (gold-to-gold delamination). Twenty percent of the devices for each TFN were allowed to have pull strengths of 8 to 12 g.

Bonding test results are shown in Figure 11, category A. The results were somewhat unexpected, because all beam lead devices tested were within the required production limits. Average pull strengths were around 25 g for all stripping conditions. Minimum pull strengths were also within required limits; no D failure bond delaminations were noted. These bonding results included TFNs showing gross amounts of resist on the gold surface metallization. Categories A through H (Figure 9) were tested; they consisted of TFNs stripped at 200 to 50 percent of exact strip time (T_S).

Device adhesion and pull strength did not correlate with the resist contamination conditions established in the visual examination. Those TFNs which were over stripped showed similar pull strengths to TFNs which were under stripped. It was concluded that resist residues were not contributing to bonding problems even if some were inadvertently left on the TFN surface.

Figure 11. Bonding and Auger Analysis on TFN Surface Gold Metallization Subjected to Various Stripping Conditions

Scanning Auger Analysis

Auger analysis was used in addition to visual methods to detect residual amounts of resist on TFN samples. TFNs representing all stripping conditions were tested by this method. The Auger operator sampled all surfaces present on the TFNs for resist residues, that is, the conductor, resistor, and ceramic material. Any residual resist would show up on the Auger charts as carbon peaks. A problem normally encountered when looking for carbon is that handling and packaging contact with the TFN will leave small amounts of organic contamination on the TFN surface which will result in carbon indications. Therefore, an initial reading was taken followed by a 10 second sputtering to remove any extraneous contamination from handling and packaging; the second reading obtained is more indicative of true conditions.

All samples tested showed strong carbon peaks initially. After 10 seconds of sputtering, the peaks were either reduced significantly or were not present. There was not a smooth transition of carbon indications from the over strip (code A) to the under strip (code H) conditions. The results generally showed surfaces over stripped had less carbon present than those which were under stripped; however, results were sporadic.

To get more quantitative results, the ratio of carbon to the surface material examined was reviewed. This ratio will indicate carbon peak magnitude with respect to the gold, tantalum nitride, and ceramic surface peaks. The carbon-to-gold ratios are shown in Figure 4B. Both presputter and post sputter results are shown in this graph. It can be seen that carbon indications were much higher (a higher ratio) for initial conditions, but they were suppressed after 10 seconds of sputtering; the gold surface was two orders of magnitude cleaner after the 10 second Auger sputtering. It is doubtful that this amount of sputtering would remove gross amounts of photoresist and the difference was probably due to handling contamination being removed from the gold surface.

Auger results obtained on tantalum and ceramic surfaces did not show similar reduction of carbon from initial to post sputter readings. Initial peaks of carbon were larger for both these materials with a small reduction after sputtering. These ratios are shown in Figure 12 for both pre- and post-sputter conditions. It was difficult to determine if any resist residue was on the substrate surface using this method of detection. Results were sporadic and did not correlate with visual indications. Most of the carbon peaks on Auger charts were very small after 10 seconds of sputtering. The reason for these results may be caused by the manner in which resist is removed from the TFN surface. Instead of being removed as a layer, it is removed by stripping until smaller and smaller areas of resist remain. If the Auger sampling

Figure 12. Auger Analysis on TFN Surfaces After Resist Was Stripped at Various Conditions

area falls between the residual resist islands remaining, a clean (no carbon) indication may be given. This would account for the sporadic results obtained in this evaluation. Consequently, the scanning Auger analysis is not considered a good technique for detecting residual resist on TFNs. It would indicate a general cleanliness if the TFN were sampled at several locations over the substrate area. However, this would be of limited significance since carbon would be detected initially from any handling or adsorbed contamination.

Spray Processing

No work was conducted on the spray processing activity originally planned for this project, and the funds allocated for that work were not spent. Higher priority production support needs precluded the development work on spray processing.

ACCOMPLISHMENTS

The formulation and operating limits of the gold etchant solution were revised to assure that the initial solution makeup is always within required values for iodine concentration and specific gravity and that the etchant will not be used for extended time. It was determined that the DI water rinse removal of iodine from thin film networks is not significantly improved by increasing the rinse time beyond 15 seconds. Nitrogen bubble burst, increased temperature of the rinse water, methyl alcohol rinse, and potassium iodide solution prerinse were shown to be effective in improving the rinse removal of iodine. As a result of this work, the production rinsing steps have been changed to three successive nitrogen bubble burst rinses of 5, 10, and 15 seconds. Production requirements for stripping wet photoresist from thin film networks were shown to be more than three times longer than necessary to assure that the photoresist was completely removed. However, even when stripping times were shortened to the point that resist residue was visibly remaining on thin film surfaces, no bond delaminations occurred when beam lead devices were thermocompression bonded to the thin film networks and then pull tested.

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THIN FILM GOLD ETCHANT FORMULATION AND RINSE
REMOVAL, M. K. Raut, Final, July 1980.

The chemistry of gold etchant solutions used in photolithography of thin film networks (TFNs) for hybrid microcircuits was reviewed. The formulation and operating limits were revised to ensure that the initial solution makeup is always within required values for iodine concentration and specific gravity and that the etchant will not be used for an extended period of time. Rinsing procedures for removal of the gold etchant from the TFNs were evaluated.

ELECTRICAL: Gold Etch

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Increasing the rinse time beyond 15 seconds in deionized water does not significantly improve the removal of iodine. Nitrogen bubble burst, increased temperature of the rinse water, methyl alcohol rinse, and potassium iodide solution prerinse were shown to be effective in improving the rinse removal of iodine. Production requirements for stripping time for wet photoresist were shown to be more than three times longer than necessary to ensure that the photoresist was completely removed.

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