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CHARACTERIZATION OF A CHROME-GOLD
THIN FILM DEPOSITION PROCESS BY
AUGER ANALYSIS

Technological Spinoff Report

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August 1974

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**Kansas City
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CHARACTERIZATION OF A CHROME-GOLD THIN FILM DEPOSITION PROCESS
BY AUGER ANALYSIS

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August 1974

Prepared by F. A. Clay, D/814

A chromium-gold thin film deposited onto tantalum-nitride-coated aluminum oxide substrates was investigated in terms of deposition parameters, electrical resistivity, adhesion, and thermocompression bondability. Thermocompression bondability was acceptable for all films in the as-deposited condition; was marginal to unacceptable for stabilized films; and was (again) acceptable for films which had been chemically etched after stabilizing. Auger Electron Spectroscopy was used to correlate degraded bondability with the presence of a chromium oxide contaminant formed on the gold bonding surface as a result of thermal stabilization. Production process parameters were established.

THE BENDIX CORPORATION

KANSAS CITY DIVISION

KANSAS CITY, MISSOURI

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SUMMARY

A study was made of adhesion, electrical resistivity, and thermocompression bondability of chromium-gold films which had been deposited on tantalum nitride-coated aluminum oxide substrates. The results indicate substrate temperature must be controlled to within $300 \pm 10^\circ\text{C}$; chromium deposition rate must be controlled to within 1 to 3 angstroms/second (0.1 to 0.3 nm/s); and gold deposition rate must be controlled to within 30 ± 5 angstroms/second (3 ± 0.5 nm/s) to obtain adequate resistivity and thermocompression bondability.

Electron beam evaporation was used for the study. The temperature profile and thickness uniformity of the deposition fixture were determined before the investigation was started. Thickness monitors were made from both glass and tantalum nitride-coated aluminum oxide substrates. All bonding, resistivity, and adhesion samples used tantalum nitride-coated aluminum oxide substrates.

The films were deposited at gold evaporation rates of 20, 30, 40, and 50 angstroms/second (2, 3, 4, and 5 nm/s); chromium sublimation rates of 0.5, 1, 3, and 5 angstroms/second (0.05, 0.1, 0.3, and 0.5 nm/s); and substrate temperatures of 150, 200, and 300°C . The gold films averaged 30,000 angstroms (3000 nm) thickness and the chromium films averaged 250 angstroms (25 nm). Film thickness was measured using both beta backscatter and a stylus profilometer.

The adhesion of the chromium and gold films to the substrate was evaluated using a tape test and was found to be acceptable for all deposition conditions.

Electrical resistivity of the film was measured with a conventional four-point probe. Values ranged from a minimum of 2.59 microhm-centimeters for a substrate deposition temperature of 150°C to a maximum of 3.57 microhm-centimeters for a substrate deposition temperature of 300°C .

Thermocompression bondability was evaluated using both solid gold wire and gold plated lead frames. Auger Electron Spectroscopy (AES) was used to monitor the surface of the film. The bondability of all as-deposited films was satisfactory in that there were no failures in the bond interface. Bondability was found to degrade significantly on films that had been processed through a resistor stabilization cycle of 300°C for 2 hours in air. The stabilized films exhibited 14.4 to 100 percent bond delaminations, depending on the conditions of deposition.

The degradation in bondability was attributed to the presence of chromium oxide on the surface of the gold films. Previous work had shown that chromium diffuses rapidly throughout the gold film during the gold evaporation process and during 300°C stabilization. AES testing verified chromium oxide was not present on the as-deposited mirrors but was present on all stabilized parts. The bondability of the stabilized films was restored by using a special prebond etch to remove the chromium oxide. No bond delaminations were detected on etched parts.

Films exhibiting the best bondability after stabilization were produced at evaporation rates of 1 angstrom/second (10 nm/s) of chromium; 30 angstroms/second (3 nm/s) of gold; and a substrate temperature of 300°C. Films deposited at these conditions do not require a special etch before bonding. The conditions do not coincide with the minimum resistivity; however, the resistivity obtained is satisfactory. The results of this investigation permitted selection of chromium-gold deposition parameters for hybrid microcircuit production.

DISCUSSION

SCOPE AND PURPOSE

This investigation determined optimum operating parameters for a new electron beam evaporation unit. Evaporation rates of chromium and gold and substrate temperatures were varied to determine their effect on film adhesion, electrical resistivity, and thermocompression bondability. This work was funded on Process Development Order 6984682.

ACTIVITY

Deposition Process

Hybrid microcircuits produced at Bendix Kansas City utilize a gold-chromium-tantalum nitride metallization system on an aluminum oxide substrate. The tantalum nitride resistor network is sputter coated on the cleaned substrate. A few hundred angstroms of chromium are then evaporated onto the tantalum nitride surface, followed immediately by an application of several thousand angstroms of gold. The gold is used for the conductor pattern, while the chromium promotes adhesion between the gold and tantalum nitride. The gold conductor network must be adherent, thermocompression bondable, and meet the required electrical properties. Bondability has been one of the principal problems with the chromium-gold metallization system.

Before a newly purchased electron beam evaporation unit with planetary fixturing could be turned over to production, its optimum operating parameters had to be established. The effects of the operating variables of deposition rate (both chromium and gold) and substrate temperature on adhesion, conductivity and thermocompression bondability of the film were investigated.

Chromium-gold films were deposited on both glass and tantalum nitride coated aluminum oxide substrates at gold evaporation rates of 20, 30, 40, and 50 angstroms/second (2, 3, 4, and 5 nm/s); chromium sublimation rates of 0.1, 1, 3, and 5 angstroms/second (0.05, 0.1, 0.3, and 0.5 nm/s); and substrate temperature of 150, 200, and 300°C. The gold films averaged 30,000 angstroms (3000 nm) thickness, and the chromium films averaged 250 angstroms (25 nm).

After deposition, the thickness of the film was measured using beta backscatter and a stylus profilometer. The adhesion was checked using the standard tape test and the resistivity of the film was measured with a conventional four-point probe.

There were no adhesion failures encountered for any condition tested. The thickness data verified that the gold films were nominally 30,000 angstroms (3000 nm) thick. The resistivity results are shown in Table 1. Little variation in resistivity was caused by deposition rate; therefore, the values shown are the average of all rates at one substrate temperature.

Table 1. Results of Resistivity Measurements

Substrate Temperature (°C)	As-Deposited Resistivity ($\mu\Omega/\text{cm}$)	As-Stabilized Resistivity ($\mu\Omega/\text{cm}$)
150	2.62	3.01
200	2.86	3.11
300	3.45	3.45

There is a much larger variation in as-deposited films than in the stabilized ones. It is felt that the variation of 3.01 to 3.45 microhm-centimeters is not significant in that the electrical functions of the circuit would not be affected by selecting any of the above conditions.

Film Conditions

Three basic thin film conditions were evaluated: as-deposited, as-stabilized, and prebond etched. As implied by the name, the as-deposited condition refers to films, however produced, immediately after their removal from the vacuum deposition system. They received no further processing other than routine cleaning prior to thermocompression bonding.

The as-stabilized condition defines films which, after removal from the deposition system, were given the additional processing step of a 300°C, 2-hour bake in air. This heat treatment is used to stabilize and rough trim the exposed tantalum nitride resistor network in the thin film hybrids. Except for routine cleaning for thermocompression bonding they receive no further processing.

The prebond etched condition is defined as follows: after stabilization, the films were etched in ceric ammonium nitrate* (CAN) for 10 minutes to remove the chromium oxide bonding

*Composition of etch: 164 grams ceric ammonium nitrate, dissolve in 200 ml DI water, 130 ml concentrated HNO_3 , dilute up to 1 liter with DI water. Referred to in the report as CAN etch.

contaminant formed during stabilization. Previous studies have shown chromium diffuses rapidly through the gold film during the 300°C, 2-hour bake cycle producing chromium oxide on the surface of the gold. Details regarding the prebond etch process are described elsewhere. After prebond etching, they received no further processing other than routine cleaning for thermo-compression bonding. No photolithographic processing was performed on any of the films used in this evaluation.

Prebond etching was performed on three substrates from each of the 14 basic depositions. The amount of chromium removed during this procedure was determined by atomic absorption analysis of the etchants in an attempt to correlate bondability results with amount of surface chromium. The results are shown in Table 2.

Table 2. Correlation of Bondability and Surface Chromium by AES

Deposition Rate		Substrate Temperature (°C)	Amount of Chromium Removed (Micrograms)
Gold (Å/sec) (n/s)	Chromium (Å/sec) (n/s)		
20 (2)	1 (0.1)	150	10.5
30 (3)	1 (0.1)	150	8.1
40 (4)	1 (0.1)	150	7.1
50 (5)	1 (0.1)	150	8.1
20 (2)	1 (0.1)	200	13.1
30 (3)	1 (0.1)	200	18.1
40 (4)	1 (0.1)	200	15.5
20 (2)	1 (0.1)	300	10.4
30 (3)	1 (0.1)	300	10.5
40 (4)	1 (0.1)	300	13.4
30 (3)	1 (0.1)	200	16.9
30 (3)	3 (0.3)	150	13.5
30 (3)	5 (0.5)	150	14.6
30 (3)	0.5 (0.05)	150	21.3

As shown, there is no clear correlation between amount of chromium removed during CAN etching and metallizing conditions. There was also no correlation with bondability data.

This analysis shows that only about 10 percent of the total amount of chromium deposited is removed in the CAN etch process. The remainder is within the gold and at the tantalum nitride-gold interface.

Bondability

The bondability of the gold conductor films was based on an evaluation of gold fine wire bonds with a diameter of 0.001 inch (0.03 cm) and gold plated lead frame bonds with cross sections measuring 0.005 inch by 0.015 inch (0.13 by 0.38 mm). Approximately 2000 thermocompression bonds, half fine wire and half lead frame, were made to seventy-five 1.5 inch by 1.5 inch (38 mm) aluminum oxide substrates. For the fine wire case, thermocompression bonds were made to the gold films utilizing conventional equipment with a special bonding tool. Bond schedules were determined by standard production techniques. Wire loops were then pulled to destruction in tension. The films were defined as bondable if all bonds failed as wire failures. The film was defined as nonbondable if a bond failed as a delamination, that is, if the fracture occurred between the gold film and the wire (Figure 1). If a bond failed in any mode other than the above two, it was considered no test.

Lead frame bondability was based on failure mode and strength. Gold plated lead frames were thermocompression bonded with a 0.010 inch (0.25 mm) wide tool and pulled to destruction in a 90 degree peel test (Figure 2). The films were defined as bondable if: the average of the peel strengths was greater than or equal to 1.5 pounds (6.7 N), individual peel strengths were greater than or equal to 0.75 (3.3 N) pounds, and 60 percent or more of the total failure modes were heel failures. The films were defined as nonbondable if the average peel strength was less than 0.1 pound (4.4 N) or an individual peel strength was less than 0.75 pound (3.3 N). Gold films with lead frame bondability results between these two criteria were given further evaluation. Again, if a bond failed in any mode other than the above, it was considered no test.

The bondability results are shown in Table 3. Only the data concerning stabilized films is shown because in all cases; the as-deposited and CAN etched parts showed no delaminations of either wire or lead frame bonds. The data in Table 3 indicates that a high substrate temperature during deposition reduces the need for CAN etching before bonding. It also indicates that a deposition temperature higher than 300°C may allow elimination of the CAN etching operation.

As stated previously, the degradation of thermocompression bondability of stabilized films was caused by chromium oxide on the surface. Auger Electron Spectroscopy (AES) was used to examine the gold bonding surfaces for the presence of chromium oxide and to attempt to correlate the amount present with bondability. It was hoped peak analysis of the AES spectra in combination with the atomic absorption analysis would allow an exact determination. No exact correlation was found.

Figure 1. Wire Bond Failure

Films in the as-deposited, as-stabilized, and prebond etched conditions from each run were analyzed at instrument parameters of 5000 electron volts primary energy, 50 microamperes analyzing current, 10 electron volts modulation; and, if sputtered, 1000 and 2000 electron volts argon ions. Three principal observations can be obtained from the results summarized in Table 4 and Figures 3, 4, and 5 for the as-deposited condition: surface chromium was not detected at either 150 or 200°C substrate deposition temperatures and only trace amounts at a substrate deposition temperature of 300°C; for all depositions, chromium was detected on the surface of the as-stabilized films; and chromium was never detected on the surface of films which had been given the prebond or CAN etch.

Figure 2. Lead Frame Bond Failure.

In addition to surface analysis, AES was used to determine elemental concentration profiles for films in the as-stabilized condition. Specifically, the relative concentrations of chromium, oxygen, carbon, and gold were determined as a function of depth below the original gold surface. Figure 6 is typical of the results obtained for each run. Relative concentrations are plotted on the vertical axis (arbitrary units) with sputter time in minutes plotted along the horizontal axis. Actual data points are indicated by the various symbols which are connected by straight lines.

As indicated in Figure 6, base line surface concentrations were obtained prior to beginning of sputtering. Basically, as the distance from the original free gold surface increased, the concentrations of chromium, oxygen, and carbon decreased from surface values to those characteristic of the bulk film while the gold concentration increased. The carbon concentration dropped very rapidly from its surface value indicating it may have been picked up during routine handling or storage of the films.

The chromium concentration increased above its surface value during initial sputtering followed by a decrease to a bulk film value; this behavior occurred in all as-stabilized films. A possible explanation of this is that the sputtering very rapidly removed the carbon which was masking the chromium, thereby exposing a surface of higher chromium concentration. The rise

Table 3. As-Stabilized Bondability

Deposition Rate		Substrate Temperature (°C)	Lead Frame Heel Bonds Failure (Percent)	Wire Bonds Wire Break (Percent)
Chromium (Å/sec) (nm/s)	Gold (Å/sec) (nm/s)			
1 (0.1)	20 (2)	150	18.8	86.6
1 (0.1)	30 (3)	150	25.6	96.0
1 (0.1)	40 (4)	150	54.6	94.6
1 (0.1)	50 (5)	150	38.5	97.5
1 (0.1)	20 (2)	200	25.4	96.0
1 (0.1)	30 (3)	200	23.7	93.0
1 (0.1)	40 (4)	200	36.2	97.0
1 (0.1)	20 (2)	300	82.1	100.0
1 (0.1)	30 (3)	300	85.6	100.0
1 (0.1)	40 (4)	300	40.2	98.6
1 (0.1)	30 (3)	200	25.4	90.0
3 (0.3)	30 (3)	150	24.7	100.0
5 (0.5)	30 (3)	150	0	100.0
0.5 (0.05)	30 (3)	150	0	100.0

in gold concentration with sputtering time is consistent with the removal of chromium, oxygen, and carbon, yielding a surface of higher gold concentration. Also, the essentially simultaneous decrease in chromium and oxygen concentration with distance from the original surface suggest that they are chemically combined as chromium oxide.

An attempt was made to correlate the thickness of the chromium oxide contaminant with thermocompression bondability of as-stabilized films. This was based on the possibility that a particular set of deposition parameters may result in an oxide contaminant which could be broken up by the bonding operation. Since concentration profiles similar to Figure 6 were obtained for each of the nine basic deposition conditions, an estimate was made of the relative thicknesses of the chromium oxide contaminant. For this calculation, thickness was defined as the time between the initiation of sputtering and when the

chromium concentration had a zero slope. Within the accuracy of the estimate, all stabilized films had equivalent thicknesses and no distinct correlation was established.

Table 4. AES Analysis of Gold Surface

Film Condition	Deposition Temperature (°C)		
	150	200	300
As-Deposited (nm/s Au)			
2	No	No	Yes, Trace
3	No	No	Yes, Trace
4	No	No	Yes, Trace
As-Stabilized (nm/s Au)			
2	Yes	Yes	Yes
3	Yes	Yes	Yes
4	Yes	Yes	Yes
Prebond Etch (nm/s Au)			
2	No	No	No
3	No	No	No
4	No	No	No

ACCOMPLISHMENTS

The results of this investigation permitted selection of chromium-gold deposition parameters for hybrid microcircuit production. The best operating conditions are a substrate temperature of $300 \pm 10^\circ\text{C}$; a chromium deposition rate of 1 to 3 angstroms/second (0.1 to 0.3 nm/s); and a gold deposition rate of 30 ± 5 angstroms/second (3 ± 0.5 nm/s). Films produced at this condition have good bondability and acceptable resistivity.

Text continued on Page 19.

Figure 3. Auger Graph of Deposited Specimen

Figure 4. Auger Graph of Stabilized Specimen

Figure 5. Auger Graph of CAN Etched Specimen

Figure 6. Concentration Profile of Stabilized Specimen

FUTURE WORK

Higher deposition temperatures need to be investigated to determine if bondable circuits can be produced without requiring a prebond etch. If this can be done, production bonding problems will be reduced significantly.