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BONDING DEGRADATION IN THE TANTALUM NITRIDE-CHROMIUM-GOLD METALLIZATION SYSTEM

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Prepared by N. T. Panousis, D/814 and H. B. Bonham, D/842

Thermocompression bondability in the tantalum nitride-chromium-gold metallization system is degraded because of diffusion and oxidation of chromium resulting from a 300°C two hour air bake used to stabilize the tantalum nitride resistor network. Bondability can be restored by chemically removing the contaminant with either a gold (potassium iodide and iodine) or a chromium oxide (ceric ammonium nitrate) etch treatment before thermocompression bonding. The integrity of bonds made to restored films is not degraded in tests at temperatures between -50 and 350°C for up to 200 hours. Delamination at the gold-chromium interface could not be induced by extended etching in ceric ammonium nitrate for as long as 96 hours.

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INTRODUCTION

The reliability of thermocompression bonds made to thin film networks is influenced by the condition of the bonding surfaces. Properties of these surfaces which affect bond integrity are surface finish, absorbed gases, and surface contaminants. Surface finish is not critical because thermocompression bonding subjects the metals to sufficient deformation that close interfacial gaps by material flow. Absorbed gases do not significantly influence bond integrity because the parts are normally heated before bonding, thereby removing any absorbed gases. Surface contaminants which would impair adhesion are therefore the primary factors which influence bond integrity.

Surface contaminants may be divided into two categories: foreign materials and oxide films. Foreign materials such as particles, greases, and salts can be removed by solvent cleaning. Oxide films are more difficult to remove and usually require chemical etching. This paper discusses an oxide contaminant which was found to be distributed through the top several hundred angstroms of the bonding pads and caused degraded bondability.

The resistor-conductor network studied consisted of three layers of metallization; tantalum nitride, chromium, and gold respectively deposited onto aluminum oxide substrates, see Figure 1. The tantalum nitride resistor network was produced by sputtering tantalum in a nitrogen doped argon atmosphere. Transmission electron diffraction of the films showed them to be hexagonal Ta_2N phase.¹

Conductors and bonding pads, nominally $30,000 \text{ \AA}$ (3000 nm) thick, were prepared by evaporating gold from a resistance heated source at approximately $30 \text{ \AA}$ (3 nm) per second. In order to get satisfactory adhesion of the gold film, a $200 \text{ \AA}$ (20 nm) layer of chromium was sublimed at approximately $5 \text{ \AA}$ (0.5 nm) per second on the tantalum nitride film immediately before the gold deposition. Substrates were preheated to 300°C for the tantalum nitride sputtering and to either 200 or 300°C for the chromium and gold depositions.

Reliable thermocompression bonds can be made to the as-deposited gold. However, during fabrication the resistor-conductor networks are subjected to a 300°C air bake for two hours to stabilize the tantalum nitride resistor network. Following the 300°C two hour air stabilization reliable thermocompression bonds cannot be made to the gold. The purposes of this work were to:

- Determine the identity and mechanism by which the contaminant was formed;
- Determine a technique to remove the contaminant; and
- Investigate the long term reliability of bonds made to restored networks.

Figure 1. Schematic Illustration of the As-Deposited Tantalum Nitride, Chromium, Gold Metallization System.

DISCUSSION AND RESULTS

Bondability Criteria

Bondability of gold conductor networks was based on an evaluation of gold fine wire (0.001 inch diameter) bonds and gold plated lead frame (0.005 inch x 0.015 inch-cross section) bonds. Twenty consecutive fine wire thermocompression bonds were made to the gold conductors utilizing conventional equipment with a "tailless" bonding tool. Bond schedules were determined by techniques described elsewhere.² Ball bonds were then pulled to destruction in tension as illustrated in Figure 2. The network was defined as bondable if all bonds failed as wire failures. The network was defined nonbondable if a single bond failed as a delamination, that is, if the fracture occurred between the gold network and the ball. If a bond failed in any mode other than the above two, it was considered a no test and an additional bond was pulled.

Lead frame bondability was based on failure mode and strength. Lead frames were thermocompression bonded with a 0.010 inch wide tool and pulled to destruction in a 90 degree peel test as shown in Figure 3. If the bonds had an average strength of 1.0 pound with a minimum of 0.75 pound, the network was defined as bondable. If a single bond delaminated with a strength of less than 0.75 pound, the network was defined as non-bondable. A lead which failed by a mode other than a delamination at a strength less than the 0.75 pound limit was considered a no test, and an additional lead was pulled.

FIGURE 2 - Wire Bond Criteria:

- Bondable. All bonds failed as wire failures.
- Not Bondable. At least one bond failed as a bond delamination.
- No Test. Fracture was not a wire failure of a bond delamination.

FIGURE 3 - Lead Frame Bond Criteria:

- Bondable. All bonds required more than 0.75 pound to fracture with the average greater than or equal to 1.0 pound.
- Not Bondable. At least one bond failed as a bond delamination with a strength less than 0.75.
- No Test. Failed at less than 0.75 pound and was NOT a bond delamination.

Formation and Identification of the Bonding Contaminant

Diffusion of chromium through gold films has been well documented.³⁻⁷ Therefore, it was hypothesized that chromium diffusion was the mechanism through which bonding was degraded. To test the hypothesis and to determine the extent of the degradation, resistor-conductor networks were stabilized in air for two hours at temperatures between 225 and 400°C. Following this the bonding pads were analyzed for chromium using Energy Dispersive X-ray analysis, Edax, Auger Electron Spectroscopy, AES, and Ion Scattering Spectroscopy, ISS, then evaluated for bondability. Table I summarizes the results and points to three principal observations. Firstly, there is a direct correlation between the presence of chromium on the bonding pads and the inability to make reliable thermocompression bonds. Secondly, wire bonding is seen to be more sensitive to the contaminant in that unreliability occurred at a lower temperature than for lead frame bonding. Thirdly, the present stabilization cycle for the resistor network, 300°C for 2 hours in air, is seen to be in the transition region and generally considered unreliable for thermocompression bonding.

Table I Correlation of bondability with detection of chromium for samples which received a two hour air stabilization at temperatures between 225 and 400°C

<u>Stabilization Temp</u> <u>Temp °C</u>	<u>Bondability</u>		<u>Chromium</u> <u>Detected</u>
	<u>Wire</u>	<u>Lead Frames</u>	
225	Yes	Yes	No
250	Marginal	Yes	No
300	No	Marginal	Marginal
350	No	No	Yes
375	No	No	Yes
400	No	No	Yes

The identity of the bonding contaminant was further established by use of Electron Spectroscopy for Chemical Analysis, ESCA, which is an analytical technique capable of identifying the chemical state of an element. Examination of a nonbondable gold film by ESCA established the presence of a chromium oxide on the bonding surface although the lack of standards precluded the identification of the exact oxidation state. The ESCA conclusion was consistent with the inference which could be made from the Auger spectra. Therefore, the diffusion and oxidation of chromium on the surface of the bonding pads was concluded as the mechanism through which bonding was degraded.

First order approximations were used to construct a model for the chromium concentration within the gold conductor film. The model assumed that the films were fully dense so that, for example, a chromium thickness could be calculated by the ratio of the weight of chromium to the product of the network area and the density of chromium. Additionally, the model considered only diffusion of the chromium within the gold films, specifically excluded were any interactions with the tantalum nitride resistor network or the aluminum oxide substrate. Finally, the details of this profile reflect the particular combination of processing parameters defined above.⁴⁻⁶

Figure 4 shows the chromium concentration profile determined for a 2.6 cm x 2.6 cm network stabilized in air at 300°C for two hours. Units were chosen such that the area under the curve is equal to the total amount of chromium. The analysis used to construct the concentration profile was as follows. Auger electron spectroscopy and ion scattering spectroscopy were used to in situ sputter through the chromium oxide layer in an as-stabilized network. The Auger technique indicated that the chromium oxide

Figure 4 . Profile of Chromium Concentration Within the Gold Conductor Following the 300°C/2 Hour Air Stabilization.

was dispersed in the top 2000 Å (200 nm) of the gold film whereas ion scattering indicated a depth of 500 Å (50 nm). Atomic absorption spectroscopy determined that of a total of 148.5 µg of chromium, 12.6 µg were dispersed in the upper 500 to 2000 Å (50 to 200 nm) of the gold film 25.3 µg were at the original location, and 110.6 µg were dispersed in the bulk of the gold film.

Removal of the Bonding Contaminant and Restoration of Bondability

Chemical etching was used to remove the chromium oxide from the gold bonding surfaces. The composition of the metallization system suggested two approaches for chemical cleaning: etch the gold to remove the chromium oxide by undercutting; or etch the chromium oxide directly. In the first set of experiments, as-stabilized networks were given a gold etch treatment before bonding with potassium iodide/iodine.* This process removed approximately 2000 Å (200 nm) of gold as well as surface contaminants. Thermo-compression bondability was restored by this prebond etch; however, surface analysis of the gold showed that not all the chromium oxide had been removed. In addition, the resistivity of the gold network increased following the prebond gold etch. Therefore, direct etching of the chromium oxide was evaluated to improve the deficiencies found with the KI/I₂ etch.

Ceric ammonium nitrate (CAN**), an etchant specific to chromium and

* Au Etchant: 63.46 grams I₂; 100 grams KI; dissolve in 200ml DI water, dilute up to 500 ml with DI water.

** Cr Etchant: 164 grams ceric ammonium nitrate, dissolve in 200ml DI water, 130ml conc HNO₃; dilute up to 1 liter with DI water.

chromium oxide, was evaluated for the direct removal of the contaminant.

The experiments consisted of submitting resistor-conductor networks to three different treatments. The first group were as-fabricated; the second were stabilized in air for two hours at 300°C but were not prebond etched; while the third group were stabilized and then given a prebond etch with CAN four times ranging between 10 minutes and 16 hours (overnight). All networks were then lead frame and fine wire bonded and surface analyzed. Table II summarizes the results. A correlation was again exhibited between the presence of chromium and the inability to make reliable thermocompression bonds. Note also that as little as ten minutes was satisfactory to remove the chromium oxide and restore bondability.

TABLE II Restoration of thermocompression bondability by use of a ceric ammonium nitrate prebond etch

<u>Sample Condition</u>	<u>Bondability</u>		<u>Chromium Detected on Gold Bonding Surface</u>	<u>Amount of Chromium Undercutting Based On Original Gold Path Width or 5 mils (mils)</u>
	<u>Fine Wire</u>	<u>Lead Frame</u>		
As Fabricated Network	Yes	Yes	No	0.21
Network Stabilized in Air for 2 hours at 300°C	No	No	Yes	0.68
Network Stabilized in Air for 2 hours at 300°C then prebond etched in CAN for the following times				
10 minutes	Yes	Yes	No	
1 hour	Yes	Yes	No	0.40
2 hours	Yes	Yes	No	0.80
3 hours	Yes	Yes	No	0.31
16 hours	Yes	Yes	No	0.52

To further characterize the CAN prebond etch process, the etchants used in determining the entries in Table II were analyzed for the amount of chromium by atomic absorption spectroscopy. The significant result shown in Figure 5, was that the amount of chromium removed was independent of time. It was expected that the amount of chromium removed would increase with increased etching time due to such things as chromium undercutting. Therefore, the amount of chromium undercutting following the CAN prebond etch was measured with the results included in Table II. The undercutting results are consistent with the atomic absorption results for chromium content in that neither shows a dependence on the time of prebond etching.

Reliability of Bonds Made to Restored Networks

Since chemical etching only removes chromium oxide from a surface, restored resistor-conductor networks may experience additional contamination during circuit operation. It is of little immediate interest, from a bondability point of view, that gold surfaces can become contaminated after circuit fabrication, but that such contamination may degrade bond integrity is important. To determine the influence of continued chromium diffusion on bond integrity and to simulate product field conditions, bonds to restored films were exposed to high temperature storage, temperature cycling, temperature storage under rated power, and storage at 75°C at 100% relative humidity. The results and a brief explanation of the tests performed are listed in Table III. Neither fine wire nor lead frame bonds degraded. Although not listed in the table, bond integrity was evaluated periodically by pull testing throughout the duration of each test. Within experimental error, the periodic pull strengths determined were equivalent to the strength prior to environmental stressing.

Figure 5 Relation Between Time of Ceric Ammonium Nitrate Prebond Etch and Amount of Chromium Removed.

TABLE III Summary of bond integrity tests performed on resistor-conductor networks which had been stabilized in air at 300°C for 2 hours then prebond etched with ceric ammonium nitrate

<u>Test</u>	<u>Description</u>	<u>Bondability Criteria Met</u>	
		<u>Wire</u>	<u>Lead Frame</u>
Temp Storage	350°C/200 hours in air	Yes	--
Temp Cycling	100 cycles; -50 +90°C at 15°C/minute	Yes	Yes
Power Burn-In	96 hours at 110°C under rated power dissipation	Yes	Yes
Humidity	75°C at 100% Relative Humidity for 96 hours	--	Yes

A second reliability consideration is the possibility of adhesion loss between the gold conductor network and the tantalum nitride resistor network. Specifically, does the ceric ammonium nitrate prebond etch treatment remove the chromium from between the gold and the tantalum nitride thereby inducing delamination of the resistor-conductor network? The undercutting measurements shown in Table II and the chromium concentration profile shown in Figure 4 established that chromium is present between the gold and tantalum nitride films following CAN prebond etching. In addition, no cases of network delamination were observed in the destructive pull test of wire and lead frame bonds made to the ceric ammonium nitrate restored networks referred to in Tables I, II, and III (these networks also passed the conventional tape test for adhesion). As an extreme overtest, networks were given a 96 hour prebond etch treatment with ceric ammonium nitrate followed by fine wire and lead frame bonding. Again network delamination

was not observed in the destructive pull tests. Therefore, network adhesion was not degraded to the extent that it was observed to be the weakest member in a thermocompression bond.*

*Experiments are in progress to utilize the noise generated at the chromium-gold interface to monitor adhesion between the two films.

CONCLUSIONS

Three principal conclusions were drawn from this study of the thermocompression bondability of the tantalum nitride-chromium-gold metallization system.

- The diffusion and oxidation of chromium which results from a 300°C two hour air bake used to stabilize the tantalum nitride resistor network was established as the mechanism through which bondability was degraded. Use was made of several analytical techniques including Auger electron spectroscopy, ion scattering spectroscopy, atomic absorption spectroscopy, and electron spectroscopy for chemical analysis to arrive at this conclusion.
- Thermocompression bondability of the gold conductor networks could be restored by chemically removing the contaminant with either a gold (potassium iodide/iodine) or chromium/chromium oxide (ceric ammonium nitrate) prebond etch treatment. The potassium iodide/iodine prebond etch treatment was shown to leave some chromium oxide on the gold bonding surfaces, whereas the ceric ammonium nitrate prebond etching completely removed the chromium oxide from the bonding surfaces.
- The integrity of bonds made to restored films was not degraded in tests which included storage in air at temperatures up to 350°C for 200 hours, power burn-in at rated power, temperature cycling 100 times between -50°C to +90°C and humidity tests. Additionally network delaminations at the gold-chromium interface could not be induced by extended etching in ceric ammonium nitrate for up to 96 hours.

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