METAL MIGRATION FAILURES IN A HYBRID DEVICE: INTERACTION OF PACKAGE MATERIALS, PROCESS RESIDUALS, AND AMBIENT GASES

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This paper presents a case history of a failure analysis performed on hybrid devices that [illegible] failures during thermal cycle with bias. Electrical testing revealed resistive shorts between Vcc and ground bond pads on integrated circuits within the package. A dendritic growth containing gold and copper extended from Vcc to ground across the surface of the passivation. Crystalline-like corrosion products were observed on the bond pads. The failure mechanism is shown to be an electrochemical corrosion reaction within the hybrid.

Hybrid devices can contain reactive chemical species from outgassing of organic adhesives, residual cleaning solvents, and other process related materials. These are present as adsorbed species and as gases within the package cavity. The constituents in the package ambient can react with the surfaces of wire bonds, bond pads, and substrate metallization to form the dendritic growth and other corrosion products. We have observed copper migration through a reaction of the hybrid package atmosphere and copper oxide present on the surface of the thick film gold substrate metallization.

We describe the failure analysis flow used in identifying the cause of the corrosion reactions as a result of processing. The paper concludes with correction actions to be taken to alleviate the conditions that lead to the observed failures.

INTRODUCTION

Metal migration is a common failure mode in microelectronic devices. It may cause electrical leakage, dielectric breakdown, and resistive shorts. It is most common with silver and silver alloys, but also occurs with other metals such as aluminum, copper, nickel, zinc, tin, lead, and gold (1-5). We have observed a dendritic growth that caused resistive shorts between adjacent Vcc and ground bond pads on IC devices within a hybrid package during temperature cycling with electrical bias. The dendritic growth contained both gold and copper. The mechanism for gold migration appears to be an anodic dissolution of the Vcc bond wire (6-7). The source of the copper is the thick film conductor on the hybrid substrate. Thick film gold pastes typically contain copper oxide to increase the adhesion strength to the ceramic substrate (8). We provide data suggesting the possible formation of volatile copper bearing complexes within the package ambient. In addition, a crystalline-like corrosion product was also found on all other bond pads in the device. We postulate mechanisms for the gold, copper, and aluminum corrosion based on chemical reactions of the process-related materials. This case of metal migration is unique because the condensed electrolytic film may contain primarily ammonia rather than moisture.

Package hermeticity is designed to protect the internal electronic components from harsh environmental conditions. However, hermetic packages entrap process residuals and outgassing products from organic adhesives, (i.e., ammonia, methanol, and moisture), getters, and other materials (9-13). The hybrid construction materials, hybrid processing, integrated component design, and environmental testing resulted in electrical failures caused by dendritic growth. For example, the adjacent location of the ground and Vcc bond pads is an undesirable IC design feature in this application. In addition, the incomplete removal of epoxy outgassing products and cleaning solvents created a package atmosphere which led to an electrochemical corrosion reaction. The reaction was driven by electrical bias and temperature cycling (-65 to 150°) during environmental screening. The materials used in the failed device were a silver filled epoxy, Ablestik 84-1, a non-conductive staking epoxy, Ablestik 84-3, and a substrate attach epoxy, Ablefilm 550K. The substrate attach epoxy has an amine as a curing agent. Solvent rinses were performed with a solvent mixture containing Freon TF, Methylene Chloride, Methanol, and Cyclopentane.

The purpose of this failure analysis is to understand the mechanisms for the corrosion reactions, so that corrective actions could be made to prevent similar failures in the future. If volatile copper complexes had formed, this would represent an important reliability concern with the increasing use of thick film copper pastes and other copper metallization schemes. The failure analysis process flow included: Residual Gas Analysis (RGA), of the package atmosphere; internal inspection by light microscopy, Scanning Electron Microscopy (SEM); materials analysis by Energy Dispersive X-ray Microanalysis (EDX), and Auger Electron Spectroscopy (AES).

FAILURE ANALYSIS

Internal Atmosphere

Residual Gas Analysis per Mil-Std-883, Method 1018, Procedure 1 is an extremely valuable technique in the failure analysis of hermetic packages. RGA yields information of the package seal integrity and the levels of moisture in the cavity (14). In addition, information on outgassing from epoxies, solvent residuals, and the effect of thermal stress can be determined. RGA identifies the constituents within the package cavity. Information on the chemistry of corrosion reactions can be inferred from RGA data.

The results of the RGA testing on the virgin (prior to temperature cycling/electrical burn-in) and failed devices are listed in Table I. RGA did not reveal any significant differences between virgin and failed hybrids. The package was sealed in a nitrogen-helium atmosphere, and the data shows that the package remained hermetic. Moisture levels are well below the Mil-Std limit of 5000 ppm. A significant amount of ammonia was detected. The ammonia is a by-product of the substrate attach epoxy cure. Methanol was detected, and has several potential sources. The cleaning solvent contains several percent methanol. Outgassing of methanol has been reported for several of the epoxies used in this hybrid (9-11).

Table I
RGA Results for Virgin and Failed Hybrids

Detected	Failed	Virgin
Nitrogen (%)	84.3	67.6
Oxygen (ppm)	ND	ND
Argon (ppm)	218	<100
CO_2 (ppm)	8073	4563
Moisture (ppm)	1408	1107
Hydrogen (ppm)	955	981
Helium (%)	9.83	28.0
Fluorocarbons (ppm)	ND	ND
Ammonia (%)	3.97	3.14
Hydrocarbons (ppm)	183	228
Methanol (ppm)	7632	5652

Internal Inspection

Internal inspection was performed using light microscopy and SEM. Two forms of contamination were observed on the surface of two die in the hybrid. The first was a dendritic growth extending from the bond pads across the passivation, Figure 1. The extent of the dendritic growth was particularly heavy between the Vcc and ground bond pads. Some of the failed devices had degraded to the point that the Vcc ball bond was consumed in the corrosion reaction. The degradation appeared to a be a textbook case of the anodic dissolution of the Vcc gold ball bond. The second form of contamination was a crystalline-like growth found on several bond pads. The crystalline-like growth had an opaque appearance.

MATERIALS ANALYSIS

Dendritic Growth

EDX analysis was performed on the dendrites to determine the bulk constituents. The EDX spectra showed that the dendrites contain chlorine, gold, and copper.

Auger analysis was performed to determine the surface constituents associated with the dendrites. Auger elemental surveys yield information on the top 5 to 40 angstroms of material. The surveys of the dendrites exhibited gold, copper, carbon, oxygen, nitrogen, chlorine, and silicon, Figure 2. The passivation is a silicon nitride and may contribute the silicon, nitrogen, and oxygen in the surveys of the dendrites. The source of gold for the dendritic growth is the ball bond at the Vcc bond pad. The wirebond material is pure gold, so it is not the source of the copper associated with the dendrites. The only source of copper detected by extensive AES and EDX analysis of raw hybrid construction materials was the copper oxide used in the thick film gold paste.

Crystalline-Like Growth

EDX analysis of the crystalline material on a wire-bonded pad detected high levels of chlorine with gold, aluminum, silicon, and oxygen. Crystals were also observed on open bond pads. The EDX spectra of crystals on open pads exhibited only aluminum and chlorine.

Auger surveys of the crystals showed aluminum, chlorine, oxygen, fluorine, and carbon, Figure 3. This indicates that the crystals are associated with corrosion of the aluminum bond pads.

Other Surfaces Within the Failed Hybrid

Auger surveys were collected on bond wires, thick film substrate metallization, and on the package lid to determine the extent of copper migration throughout the package. Surveys acquired on the gold-plated package lid and gold bond wires showed significant levels of copper, chlorine, and nitrogen.

Virgin Hybrid and Stock Materials

Auger analysis was performed on a test matrix which included the following samples: a stock substrate, a stock substrate exposed to chlorinated solvents, a stock package lid, an assembled hybrid prior to lid seal, and an assembled hybrid following lid seal. The test matrix was designed to determine the effect of process steps on the materials used in the hybrid construction. The results of the analysis were as follows:

1. Exposure of raw substrate to chlorinated cleaning solvents does not elevate the chlorine levels on the surface of the thick film gold.

2. Assembled hybrids exhibited high levels of chlorine and nitrogen before and after lid seal. The chlorine and nitrogen levels on the surface of the thick film gold increase as a results of the solvent cleaning steps and epoxy curing, Figures 4 and 5. It is possible that the organic adhesives absorbed the chlorinated cleaning solvents. Chlorinated species could then have been evolved from the adhesives and reacted with the copper oxide on the thick film gold. The absence of freon and methylene chloride in the RGA data suggests that the solvents had undergone chemical decomposition reactions. The increase in nitrogen levels is from outgassing of ammonia by the substrate attach epoxy.

3. Copper migration occurs throughout the package during the lid seal process prior to electrical burn-in. Copper was detected on the package lid (only on internal side), and on other components within the hybrid. The source of copper is the thick film gold metallization. The amount of copper oxide (roughly 100-300 angstroms thick) on the surface of the metallization in the raw substrates is very sensitive to firing conditions (time, temperature, forming gas, etc.), and the amount of copper oxide in the thick film ink (15). Ratios of copper to gold peak heights show a reduction in the amount of copper in the thick film gold ongoing from the raw substrate to the virgin hybrid to the failed hybrid, Table II. This trend suggests that the copper oxide is being consumed by reactions with constituents in the package ambient during the assembly process and electrical burn-in/temperature cycling. The trend correlates with the observed copper migration from the metallization to other areas with the hybrid.

Table II
Ratios of Elemental Composition

Sample	Copper/Gold
A. Failed Hybrid	
1. Substrate Metallization	0.09
2. Package Lid	0.13
B. Virgin Hybrid	
1. Substrate Metallization	0.16
2. Package Lid	0.06
C. Raw Substrate	
1. Substrate Metallization	0.25

Corrosion Mechanisms

Gold

The electrolytic corrosion mechanism for gold is commonly referred to as simple anodic dissolution (6,7). The electrochemical cell was established between two identical electrodes, each consisting of a gold wire bond to an aluminum bond pad. Three factors were present which allowed anodic dissolution of gold to proceed: a thin layer of condensed solvent (moisture, ammonia, and/or methanol), a reactive species such as chlorine to form an electrolyte, and electrical bias. When adsorbed ammonia combines with moisture,

ammonium ions and hydroxyl ions are formed. Positive gold bearing ions are generated at the anode (Vcc bond pad) at +5 volts. These ions migrate to the cathode, the ground bond pad, where gold dendrites are deposited. Chlorine is electrochemically active with gold, but is not consumed in the reaction. The reaction mechanism is relatively simple:

$$Au \dashrightarrow Au^{+3} + 3e^-$$

$$Au^{+3} + 3e^- \dashrightarrow Au$$

Copper

There are two possible mechanisms for the copper migration within the package. The first mechanism involves surface diffusion of copper oxide from the substrate metallization. Copper oxide and other inorganic copper complexes are soluble in ammonia. Copper oxide could have been dissolved in a condensed film of ammonia and flowed across the substrate surfaces. Temperature fluctuations during epoxy curing, lid seal, and temperature cycling may have had the effect of splattering a copper bearing solution throughout the package.

The second mechanism involves the formation of volatile copper organometallic complexes via a reaction of the copper oxide on the thick film gold with species in the package ambient. Gas-phase complexes could deposit copper throughout the package in a manner analogous to chemical vapor deposition. Volatile copper complexes such as Cu (I) B-diketonate have been used for CVD of copper on teflon (16). A diamino copper (II) acetate complex is an example of a possible reaction product of the ammonia, acetone, and copper oxide. There is very little vapor pressure data available for copper complexes. We were unable to detect any copper bearing complexes by RGA. However, the formation of volatile copper complexes is consistent with the observation of copper on most internal surfaces in the hybrid cavity.

Copper migrating to the surface of the integrated circuit by either of the above mechanisms could then participate in an electrochemical corrosion reaction. The presence of the copper bearing complexes, a reactive chemical, adsorbed moisture and ammonia, and the potential difference provide the necessary conditions for the electrochemical deposition of copper dendrites. A reaction mechanism for copper deposition cannot be proposed without further information on the mechanism for copper migration. The deposited copper was observed to "disappear" several weeks after delidding and exposure to the ambient.

Aluminum

Aluminum corrosion in the presence of moisture and chlorine is well documented (17,18). Chlorine is adsorbed to the surface of the aluminum bond pad under the influence of an electric field. The aluminum pad is in a hydrated oxide state due to the adsorption of water. Harmon gives the following mechanism for aluminum corrosion:

$$Al(OH)_3 + 3Cl^- \dashrightarrow Al(OH)_2\,Cl + OH^-$$

until the passivating surface oxide is dissolved. Next, the following reaction occurs:

$$2Al(Cl)_4 + 6H_2O \dashrightarrow 2Al(OH)_3 + 6H^+ + 8Cl^-$$

Chlorine is not consumed in the reaction, and continues to react with available aluminum and moisture. The consumption of moisture by this reaction may explain why the moisture levels detected by RGA were surprisingly low.

DISCUSSION

The primary cause for the failure of this device was the electrochemical corrosion of the Vcc gold ball bond and the subsequent formation of dendrites. At the same time, extensive corrosion of the aluminum bond pad metallization was occurring. The extent of the aluminum corrosion had not proceeded to the point of causing electrical opens at the wirebond. Copper migration throughout the package cavity was also observed, but the dendritic growth causing the shorts appeared to contain primarily gold. Since the reduction reactions of the positive copper and gold bearing ions at the cathode are competing processes, the reduction of gold and the resulting dendritic growth is favored thermodynamically by gold's higher reduction potential. Also, less copper was available for electrochemical deposition due to the nature of the copper migration. If volatile copper complexes had formed, this would represent an important reliability concern with the increased use of copper metallization schemes.

The relative humidity is one of the most important factors in metal migration since electrolytic processes cannot occur in the absence of an electrolytical film. In this particular case, the package atmosphere contained relatively low levels of moisture as compared to those typically reported in the literature. However, the package ambient in the failed hybrid had high levels of ammonia (approximately three percent) which could condense at temperatures below its boiling point of -33°C. Temperature cycling to temperatures below boiling point affects the critical level of humidity. If the device is rapidly cooled, moisture, ammonia, methanol, and other solvents will condense throughout the package. Condensed ammonia and moisture would form ammonium ions and hydroxyl ions which may dissolve the copper oxide and also participate in the corrosion of the aluminum bond pads (21). One way to evaluate the critical humidity is to measure surface conductivity as functions of humidity and temperature (19). Boyer and Claussen observed that the conduction mechanism for high relative humidities is primarily through ionic conduction; however, at low relative humidities, conduction occurs through electron hopping between traps associated with adsorption sites (20). The extrapolation of such measurements to real hybrid devices is complicated by the effects of contamination and the wide variety of materials used. These considerations prohibit the determination of the exact mechanism for metal migration within the hybrid.

SUMMARY AND CONCLUSIONS

The significant results of this failure analysis are summarized as follows: (1) The resistive electrical shorts between Vcc and ground were primarily due to a dendritic growth resulting from the anodic dissolution of the Vcc bond wire; (2) Electrical bias and temperature cycling from -55 to 150°C provided the driving force behind three different electrochemical corrosion reactions, and also allowed for the condensation of ammonia and moisture on surfaces within the hybrid; (3) A reaction between constituents in the package atmosphere with copper oxide on surface of the thick film gold substrate metallization resulted in copper migration throughout the package cavity; (4) Chlorinated cleaning solvents and epoxy off-gassing products must be properly removed to prevent future occurrences of similar failures.

RECOMMENDATIONS

To prevent the occurrence of similar failures we recommend that: (1) IC designs with Vcc and ground located at adjacent bond pads should be avoided; (2) Halogenated cleaning solvents must be properly removed so that they do not contribute chlorine to the formation of an electrochemical cell; (3) Vacuum bake procedures should be developed for effective removal of epoxy outgassing species and other process residuals; (4) RGA screening can be conducted to evaluate the effectiveness of the vacuum bake procedures.

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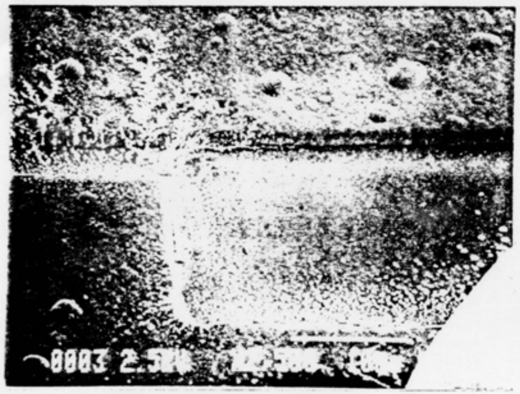

Figure 1: SEM photograph of dendrites, 2500X

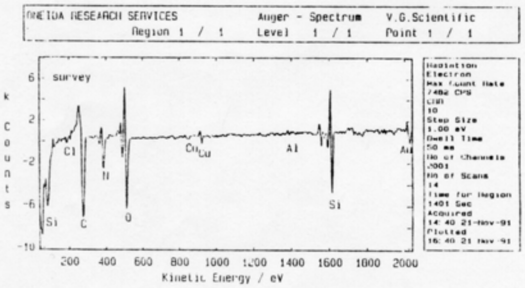

Figure 2: Auger elemental survey of dendrites

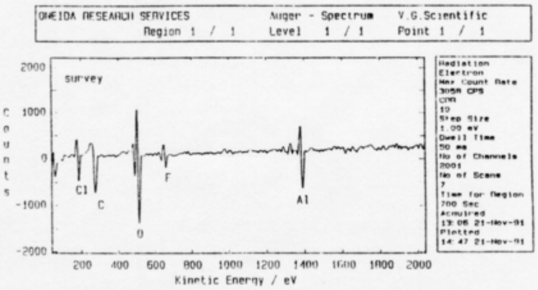

Figure 3: Auger elemental survey of crystalline-like growth

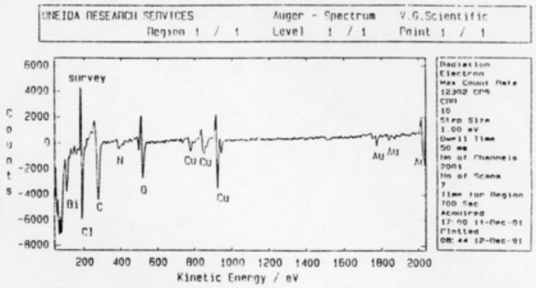

Figure 4: Auger elemental survey of substrate metallization prior to lid seal

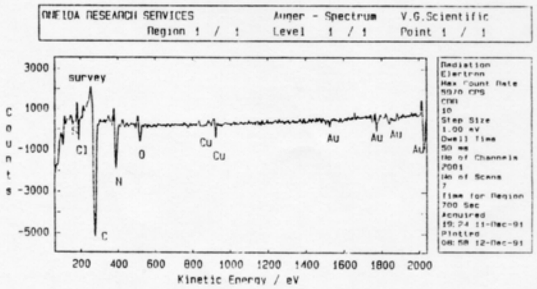

Figure 5: Auger elemental survey of substrate metallization following lid seal

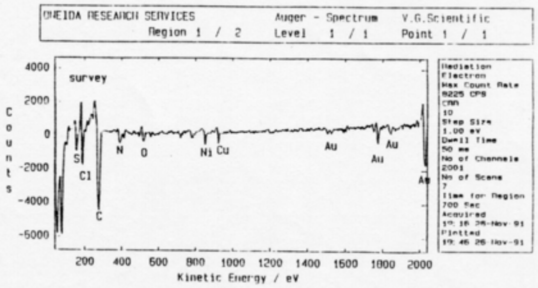

Figure 6: Auger elemental survey of package lid following lid seal