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Corrosion of SA1388-1 Diodes

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Introduction

After about 5 years of storage at Allied Signal (AS), a problem with SA1388-1 diodes was discovered. These diodes were being used in the fabrication of several components. A particular subassembly did not pass its initial performance test and the cause was traced to an unacceptable current leak rate in one of the diodes. An inspection revealed the presence of a foreign deposit that bridged the external body of the diode and presumably provided a leakage path. A preliminary investigation revealed the deposit was copper sulfide. Subsequently, the problem was shown to only be applicable to a single production lot (#1). Over 6000 of these diodes have now been electrically tested with only about 0.3% failing the 1 μ A leakage current specification (at 480 volts). However, most show some evidence of the copper sulfide material.

The physical configuration of the SA1388-1 diode is shown in Figure 1. The primary function of this device is performed by a silicon-based semiconductor that is bonded to two cylinders of tungsten. Copper headpins (Cu wire with a flat "nailhead" formed on one end) are brazed to the exposed tungsten cylinders. A toroidal ring of glass protects the Si chip. An immersion plating of Ag covers all exposed metal parts. The entire assembly is coated with black epoxy ink, and a band of green ink is applied to the cathode end. During storage, each diode was placed in a cardboard holder and secured in packages of about ten with rubber bands. In some cases, these packages were then placed in plastic bags.

Investigation

A study was performed at Allied Signal and Sandia to determine the cause and potential long-term significance of this corrosion-related degradation problem. Activity focused on analytical studies and environmental exposures. The objective of the analytical work was characterize the corrosion product and help identify the corrosion mechanism. Tools included optical microscopy, scanning electron microscopy, electron microprobe, SIMS, and x-ray diffraction. Selected Cu and Ag samples were exposed to various environments to identify potential sulfur sources. Diodes were exposed to both mildly and highly accelerated environments (40°C-85% RH and 70°C-95% RH) to determine the stability of the existing corrosion products, and to duplicate the corrosion process under accelerated conditions. For the latter study, a Class II environment was used (10 ppb H₂S, 10 ppb Cl₂, 200 ppb NO₂, 70% RH, 35°C) that, for typical industrial environments, simulates 10 years of corrosion in 2 weeks.

General Observations

Figure 2 shows SEM and backscattered electron images of the Cu-Ag-P braze alloy used to attach the Cu headpins to the W cylinders. The braze alloy consists of bright grains of Ag, medium gray grains of pure Cu, and a matrix of slightly darker, P-bearing Cu. A thin Ag layer is visible on the outside surface of the braze material in direct contact with the Ag and the Cu+P but it appears to be bridged across the corrosion pits in the pure Cu. Careful examination of SEM images and associated elemental maps revealed that there is a low density material partially filling the pits that contains Ag, Cu, P, C, and O. Overlying the metallic materials are two layers of organic materials that thin to less than 5 μ m over the braze areas (see Figure 2b). The inner layer contains particles of Al+Si+O and Cu+Cr+O. The outer layer contains Cl, S, and Ti in addition to the C. This outside layer appears to be homogeneous; it does not show discrete particles at this scale. Many of the corroded grains are filled with epoxy. All three diodes that were examined (clean, moderately corroded and, heavily corroded) exhibited similar characteristics.

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Other findings:

1. Rubber bands used in packaging at Allied Signal out-gas a sulfur-containing species that tarnish Cu and Ag coupons in days. The sulfur species is probably a thiol or mercaptan (R-SH). No tarnish was noted on Ag or Cu samples after five week of exposure to the cardboard holder material.
2. The primary portion of the sulfidation appeared to occur through pinholes and voids in the epoxy ink covering the braze material that covered the exposed portion of the tungsten slug.
3. The "flower" deposits bridging the external body of the diode are typical of copper sulfidation and oxidation through coating defects.
4. None of the components used in the manufacture of the device should have contained an active sulfur species.
5. The existing products are generally sulfur deficient and thus are not a potential source for continued corrosion. The corrosion products consist of three major groups: black dendrites; brown, shiny equant grains; and yellowish, fibrous crusts. The black dendritic crystals consist of Cu and S with a stoichiometry close to Cu_2S . The shiny, brown material contains C in addition to Cu and S. This material consists of a combination of dendrites and flat, thin plates. Chemically, this material has less Cu, much less S, and more C than the black dendrites. The yellow crusty material appears to be an organometallic copper sulfide.
6. The possible driving forces that could produce solid-state creep or movement of existing corrosion product films include voltage, temperature, chemical, and surface energy. The surface energy factor, which involves the energy of the Cu_2S -air interface vs. the Cu_2S -epoxy interface, is probably the only relevant consideration in this circumstance. SEM photos show that the deposit does not wet the epoxy surface. However, even if a driving force exists, the overriding question then becomes by what mechanism can transport occur and at what rate. In general, susceptibility to creep is related to viscosity. Overall, no evidence exists that suggests the kinetics of solid-state Cu_2S movement can be significant.
7. No further degradation or corrosion product movement was evident after five weeks of storage in the mildly accelerated environments. However, after four weeks of exposure to the Class II environment, some additional sulfidation occurred on what had been moderately corroded devices. The new product layer is somewhat duller in appearance.

Proposed Mechanism

Existence of epoxy in Cu grain voids indicates that preferential corrosion occurred during the Ag-plating operation. Solution was trapped in the gaps, and possibly, under a Ag plate top cap. After fabrication, hydrated Cu-bearing salts remained. Probably, the majority of the copper oxidation took place during the plating operation. During storage at AS, moisture condensed in the pores of the epoxy and served as a solvent and, potentially, as an electrolyte for even further corrosion. The solubilized Cu diffused to the surface and was subsequently sulfidized by the off-gas product from the rubber bands. Because Cu_2S is a reasonable ionic and electronic conductor, the sulfidation itself proceeded at the outer exposed surface, allowing the flowery deposits to form.

The probable cause of this degradation was that the P-bearing braze material that was used is not compatible with the Ag immersion plating solution (cyanide-based). In addition, the AS storage environment contained sulfur-bearing species, and the storage time was very long.

Conclusions

- The corrosion initiated during the Ag plating operation.
- Permeability of the epoxy could be the key difference in extent of corrosion on different parts.
- Water and sulfur are needed to continue corrosion.
- Most weapon environments are dry and sulfur free so further corrosion of the diodes is not anticipated.
- The existing film is relatively stable and no mechanism was observed for migration of the corrosion products.

Acknowledgment

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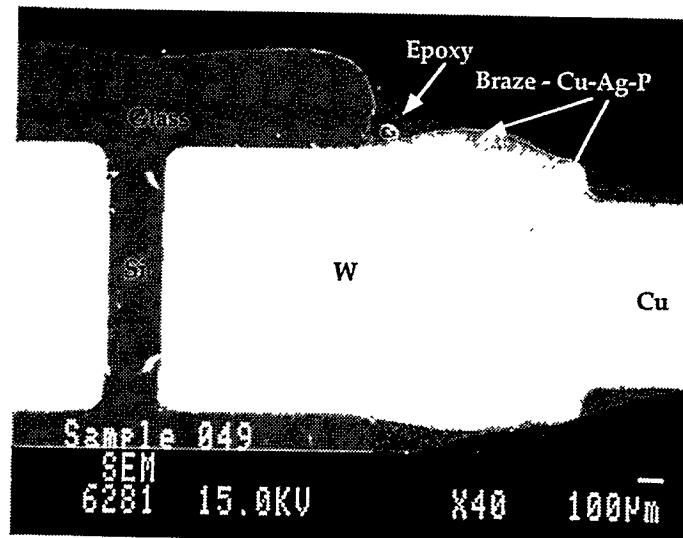


Figure 1. SEM image of the diode at 40x showing the basic construction

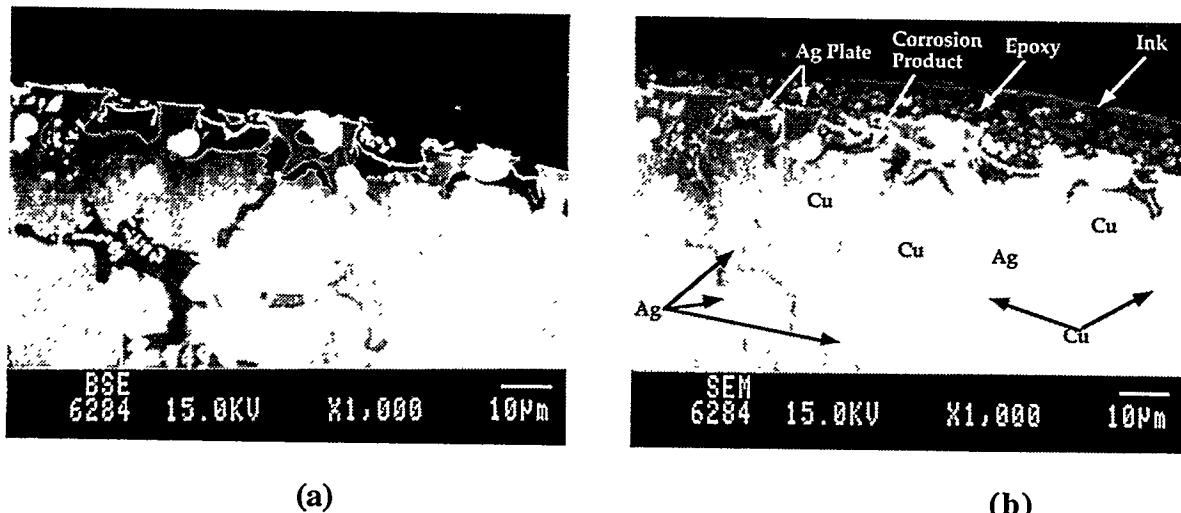


Figure 2. SEM (a) and BSE (b) images of the surface of the braze showing the three phases of the braze, the Ag-plating, the trapped Ag + Cu + P + C + O corrosion product, the epoxy, and the ink

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