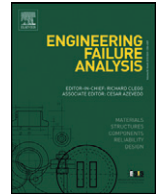




Contents lists available at ScienceDirect

Engineering Failure Analysis

journal homepage: www.elsevier.com/locate/engfailanal

Synergistic galvanic-pitting corrosion of copper electrical pads treated with electroless nickel-phosphorus/immersion gold surface finish

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ARTICLE INFO

Article history:

Received 23 January 2017

Received in revised form 24 February 2017

Accepted 6 March 2017

Available online 7 March 2017

Keywords:

Corrosion

X-ray photoelectron spectroscopy (XPS)

Microelectronics

ABSTRACT

This paper reports a study on the corrosion damage of a copper pad coated with electroless nickel-phosphorus/immersion gold in a sulfur-containing atmosphere. For this purpose, the surface and cross section of the pad showing localized corrosion products were analyzed by optical microscopy, scanning electron microscopy/energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. According to the results, slightly nickel and predominantly copper suffered from corrosion attacks, accompanied by the formation of mainly sulfide with a small fraction of sulfate. Considering the characterized configurations of the pad and corrosion products, a sequential mechanism was established to interpret the galvanic-pitting corrosion attack of both species. In this regard, the nanoporous immersion gold surface acted as the cathode in the bimetallic degradation of nickel, whereas the environmental attack of copper was accelerated because of its electrical contact with cathodic nickel and gold via the formation of a trimetallic galvanic microcell.

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1. Introduction

There are various metals currently used in microelectronics, such as Cu, Al, Au, Ag, Ni, Sn, Fe, Pd and so on, because of their appropriate electrical conductivity and solderability. Concerning corrosion, most of these metals belong to the group of active-passive metals which present suitable corrosion resistances in most circumstances, via the formation of passive films which protect the underlying metal [1,2]. However, they may suffer from serious corrosion damages under especial atmospheres, including chloride and sulfur-containing environments. For instance, Ni-based alloys present corrosion-cracking in hydrogen sulfide- and chloride-containing environments at room temperature [3,4]. Copper is also known to be susceptible to sulfur-related environmental damages, particularly in H₂S and SO₂ humid atmospheres [5–7].

The corrosion problem in microelectronics is remarkable due to the following reasons [6,8]. First, the current tendency toward the miniaturization of electrical components, regarding both dimension and spacing, leads to provoking a disruption in operation even with an insignificant damage. Second, the variety of materials used in this industry and their electrical contacts, when exposed to a corrosive atmosphere, establish galvanic cells which enhance the corrosion rate of the anodic or more-active species. Third, the existence of an electrical potential difference between the connecting components of the circuit creates an

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electrochemical corrosion potential difference, accelerating the corrosion attack in line with the current direction. On the other hand, most corrosion products having a creeping behavior are conductive enough to form undesirable short circuits between the components. Furthermore, the loss of materials due to corrosion damage in a conductor can create open circuits, where a loss of 10^{-12} g is sufficient to disturb the function of an microelectronic device [6].

Depending on the device and service environmental characteristics, the different forms of corrosion can dominate, including galvanic corrosion, gas-phase corrosion, cathodic corrosion, stray current corrosion, and fretting corrosion [6,7,9–12]. In this study, a sequential galvanic-pitting corrosion event was recognized in a copper-based pad coated with electroless nickel-phosphorus/immersion gold surface finish exposed to in a sulfur-containing atmosphere.

2. Experimental procedure

An electrical board was working in an atmosphere with the specifications summarized in Table 1. The board's function was disturbed after almost 3 years of service in this environment, accompanied by a reduction in the electrical conductivity of golden pads assembled on the board. Typically, several black spots appeared on the pad's surface, even visible to the naked eye (Fig. 1), due to environmental corrosion attack.

To analyze the corrosion failure, the cross section of the pad after mounting and grinding by sandpapers to #3000 was assessed by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Moreover, the surface of the exposed pad was characterized SEM/EDS and X-ray photoelectron spectroscopy (XPS), especially on the spots. For SEM imaging, both backscatter electron (BSE) and secondary electron (SE) modes were used to provide composition and roughness contrasts, respectively. Eventually, considering the results of the above-mentioned evaluations, a mechanism was established to describe the damage.

3. Results and discussion

The cross-sectional OM micrograph of the mounted pad is displayed in Fig. 2, inferring a thickness of about 55 μm for the pad assembled on an epoxy-based substrate. To characterize the pad's structure in more detail, the SEM/EDS study was also conducted on the related cross section, as presented in Fig. 3. An overall EDS scan on the cross section yields the presence of Au, Ni, Cu and P in the investigated area (Fig. 3c). Considering both the BSE-SEM micrograph (Fig. 3a) and the horizontally-related linear EDS scans together for the detected elements of Au, Ni, Cu and P (Fig. 3b), it is concluded that a layer of Ni-P with the mean thickness of almost 8 μm and then an Au film of about 1 μm in thickness have been deposited on the Cu-substrate pad, respectively. The individual compositions of each layer constituting the pad are also confirmed by the corresponding point EDS analyses (Fig. 3d, e and f). Hence, it is concluded that the pad is essentially composed of a Cu foil coated with electroless nickel-phosphorus/immersion gold which is one of the most-commonly used surface-finish methods to improve solderability and somewhat corrosion resistance in microelectronics [6,13]. According to Fig. 4, the top layer of the pad (Au) contains nanopores, which is typical for gold coatings obtained by immersion processes [8,12,14], whereas the Ni-P interlayer is not porous.

Fig. 5 indicates the SEM micrographs and EDS spectra of the exposed surface. The appearance of a dual contrast in the low-magnification BSE micrograph (Fig. 5a) infers a typical difference in the chemical compositions of the spots (as the corrosion damage) and intact surface. Based on this micrograph, the spots present a wide range of size from submicron to 300 μm , with a relatively rounded shape and uniform distribution on the surface. There is also another contrast although at a smaller level on the spot's its surface magnified by a BSE micrograph (Fig. 5b) which can be attributed to a small compositional and/or topographic difference. The related SE micrograph (Fig. 5c) indicates that the spot is a progression of a pit filled and overflowed with corrosion products. The non-dense particulate nature of the corrosion products is also evident in the high-magnification SE micrograph (Fig. 5d) which is in contrast to the packed and integrated feature of protective passive corrosion films. The porous and oxide/salt nature, in contrast to a packed metallic structure, of the corrosion products is responsible for a lower density and thereby more volume for them, justifying their overflow from the pit's edge. The absence of obvious cracks in the corrosion scale also reveals a relatively constant humidity level and temperature of the environment [15]. The EDS analysis (Fig. 5e) demonstrates the presence of Cu, Ni, S, O and C in the corrosion products, which can be attributed to the possible formation of the S, O and/or C-containing compounds of copper and nickel. According to the related quantitative analysis listed in Table 2, the significant amounts of Cu and S are noteworthy, which suggests the domination of copper sulfides in the corrosion product. On the other hand, the EDS analysis of the intact golden surface (Fig. 5f) indicates the existence of Au, Cu and Ni, due to the multilayer feature of the pad.

The XPS analysis was also employed in order to further characterize the exposed surface (Fig. 6). The de-convoluted spectrum of the Cu 2p orbital represents two typical peaks at 932.5 eV and 952.5 eV, which is attributed to the existence of Cu^{2+} ions

Table 1
Specifications of the service environment.

Temperature ($^{\circ}\text{C}$)	H_2S (ppm)	Humidity (%)	Cl (ppb)
15–25	30–50	50–70	~4

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