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A corrosion couple experiment reproducing the black pad phenomenon found after the electroless nickel immersion gold process

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The "black pad" phenomenon, which rarely occurs in electrolessly plated nickel–phosphorous (Ni–P) films, was reproduced. This work reports that nodular variation of the P content induces potential differences large enough to drive galvanic corrosion when the film is exposed to an electrolyte containing gold cyanide. Subsequent corrosion couple experiments using Ni–P films with different P contents demonstrated that preferential corrosion occurred at the low P side, and the propensity of forming black pad increased with the difference in P content (ΔP).

Keywords: Corrosion; Galvanization; Interface defects; Black pad

The electroless nickel immersion gold (ENIG) process has been widely used in the microelectronics packaging industry as a surface finish for solder pads. The ENIG film has good electrical conductivity, solder wettability and corrosion resistance [3–6]. However, the film is susceptible to a critical bonding failure problem, named the "black pad phenomenon", during the soldering stage, which follows the ENIG process. Reported characteristics of black pads include the presence of mud cracks, major/minor spikes [1,3] and P-enrichment. However, the difficulty of reproducing black pads out of pure chemicals is a barrier to the understanding of the phenomenon.

Suggested mechanisms of the black pad phenomenon include: (i) electric current flow in printed circuit boards (PCBs) during the IG process [1]; (ii) microgalvanic cell formation due to non-uniform Au layer plating at sharp nodule boundaries [1]; and (iii) concentrated cell formation on PCBs due to varying pad size [2]. However, in real situations electric current is not applied, and the solder pads are made to a uniform size with developments in the manufacturing technology. Although the microgalvanic cell formation at the nodule boundary has yet to be proved experimentally, it would not be problematic as long as large fraction of the film area remains bondable.

In this work, large-area black pads were reproduced using pure chemicals for the first time. Corrosion couples of nickel–phosphorous (Ni–P) films with different P contents were then made, and the result verified that varying the P content across the nodule boundary could drive microgalvanic corrosion.

In the preliminary work [11], electroless plating baths of various compositions were tried, and the bath with the following composition, which showed largest amount of black pad formation (in mol l^{-1}), was utilized: $NiCl_2{\cdot}6H_2O$ (0.08), NH_2COOH (0.20), $CH_3COONa{\cdot}3H_2O$ (0.1), $NaH_2PO_2{\cdot}H_2O$ (0.28) and $(NH_2)_2CS$ (8×10^{-6}). The electroless plating was conducted at 80 ± 1 °C, and the pH of the bath was kept at 5.3. The plating solution (0.5 dm^{-3} in volume) was renewed every 30 min to ensure the chemical stability of the bath. The phosphorous content of the Ni–P film prepared to make large-area black pads was 4–5 wt.% and Cu plates with the dimension of 1×1 cm^2 were utilized as the substrate for the electroless plating. To initiate the process, contact plating with an Fe wire was made. Ni–P film/substrates were then immersed in the IG plating bath

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Table 1. Average P content of each couple obtained at different pH levels.

Corrosion couple sample	pH of EN bath		P content (mean wt.%)	
	Film 1	Film 2	Film 1	Film 2
Couple 1	4.5	5.8	12.2	8.5
Couple 2	5	5.8	10.1	8.5
Couple 3	5.8	5.8	8.5	8.5

for 1 h at 85 ± 1 °C, where potassium gold cyanide ($KAu(CN)_2$) was added.

After the IG process, the thin Au layer was removed from the Ni–P film surfaces and a Pt film was deposited. Then, scanning electron microscopy (SEM) using a scanning electron microscope equipped for energy-dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (TEM) were conducted. The spatial variation of the P content was analyzed by EDS to a resolution of 0.7 nm.

In order to verify that the variation of the P concentration in adjoining nodules of an Ni–P film can cause microgalvanic corrosion, corrosion couple experiments were conducted as follows: Ni–P films with different P contents were deposited on the top of two Cu blocks ($1 \times 1 \times 1$ cm^3) by varying the pH levels of the EN baths, and the two Cu blocks were brought into electrical contact. The pH values and the P content of the Ni–P film comprising the corrosion couple specimens are listed in Table 1 and a schematic diagram describing the specimen is given in Figure 4(a). P variations within each film of three different average P concentrations (12.2, 10.1 and 8.5 in wt.%) were ±0.4, ±0.5 and ±0.8, respectively. Any exposed Cu surfaces were sealed to avoid contact with the IG solution, and the corrosion couple samples were immersed in the IG solution. Then regions of highest current density (the shaded area in the figure) were analyzed. For the concrete demonstration of the P content difference-induced potential difference followed by the black pad phenomenon, Ni–P films with higher P contents than that of the regular black pad samples in Figure 3 before corrosion were tested to avoid the possibility of the corrosion that occurs with relative ease in the less corrosion-resistant Ni–P films with lower P contents. It should be noted that, irrespective of the actual P content, what matters is the degree of the P content difference or variation.

Backscattered SEM images of the large-area black pad specimen after the IG process are presented in Figure 1. About 60% (± 13%) of the Ni–P film area was severely corroded and major spikes were found at nodule boundaries, which were a clear indication of the black pad. In the corroded area, Au atoms deposited on the Ni–P film while Ni selectively dissolved into the IG solution, leaving regions of higher P content behind (the thin Au layer was removed before the SEM analyses). EDS analyses showed that the P content of the corroded area (~12 wt.%) was much higher than that of the bulk film (~5 wt.%), which was consistent with previous results [1]. The P-enrichment by depletion of Ni atoms from the Ni–P film during the corrosion process was accompanied by phase transformation of the film. Before the IG process the Ni–P film (5 wt.% P) was nanocrystalline, but after corrosion it had transformed into an amorphous phase [7], where minor and major spikes, called "black bands" [8], formed normal to the film surface (cf. Figure 2a).

Cross-sectional TEM analyses of the specimen shown in Figure 1(a) were performed, and selected area diffraction (SAD) patterns and EDS data were obtained from corroded and uncorroded areas to provide information on the film structure and chemical composition. Figure 2(a) is a cross-sectional TEM micrograph of the nodules of the Ni–P film affected by the black pad, which demonstrates that the nanocrystalline film became amorphous as the result of corrosion. Corresponding EDS spectra showed the presence of Cu and O in the corroded area, even though respective concentrations were much smaller than those reported by Suganuma and Kim [7]. The source of Cu contamination and the role of Cu on the black pad formation still remain unclear.

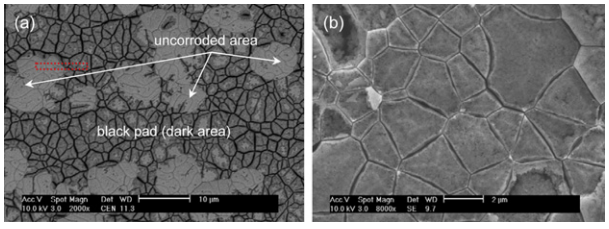

Figure 1. Backscattered electron (BSE) images of a large-area black pad specimen after the IG process: (a) showing corroded and uncorroded film areas and (b) showing spikes at nodule boundaries (reflowed with Sn 3.5Ag solder balls at 260 °C for 1 min).

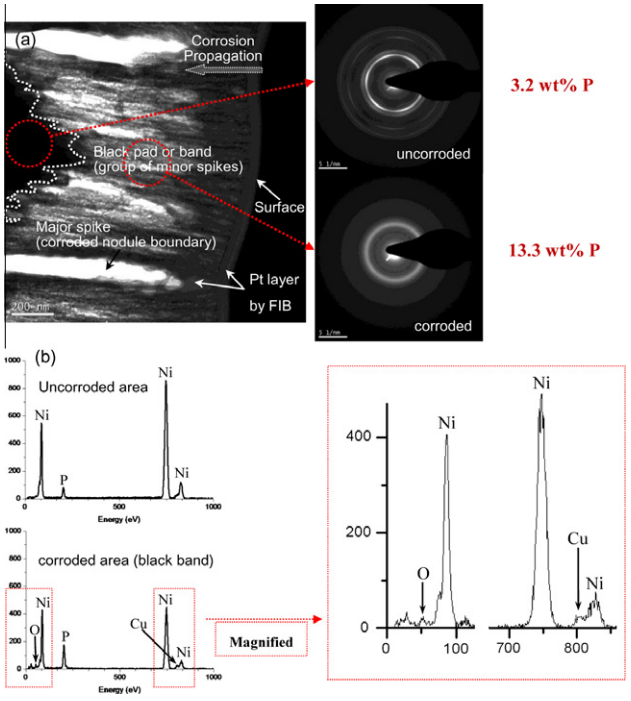

Figure 2. (a) Cross-sectional TEM image and SAD patterns of the nodules of the Ni–P film showing corroded (group of minor spikes) and uncorroded (far below the corroded surface) areas simultaneously and (b) EDS spectra from the corroded and uncorroded areas after the IG process.