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Short Communication

Effects of pH on the Immersion Gold Process from a Sulfite-Thiosulfate Solution Based on the Electroless Ni-P Alloy Substrate

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The immersion gold process from a sulfite-thiosulfate solution based on electroless Ni-P alloy substrate with 9% P content was investigated by X-ray fluorescence spectrometer, atomic force microscopy and open circuit potential measurement. The effects of pH on the gold deposition process were also discussed. The results show that the deposition rate and open circuit potential are changed during the immersion gold process. In the range of pH (6-9), a high pH results in a positive electrode potential, a slow deposition rate, and a better surface morphology of the gold coating with a smaller surface roughness.

Keywords: Electroless Ni-P alloy, Sulfite-thiosulfate bath, immersion gold, pH

1. INTRODUCTION

The electroless nickel immersion gold (ENIG) layer has been widely used in electronic applications such as printed circuit boards (PCB) and packaging industry for its excellent electrical conductivity, corrosion resistance, and good solderability[1-6]. Generally the electroless nickel (EN) process often uses hydrated sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) as the reducing agent, the coating obtained from the EN bath is a Ni-P alloy layer. The gold coating on electroless Ni-P alloy substrate was obtained by a displacement reaction that involves Au^+ reduction and Ni atom oxidation. Therefore, the Ni-P alloy substrate was corroded during the immersion gold process. However, the excessive corrosion of EN substrate in the IG process has been known as the “black pad” defect which often causes problem solder point brittle fracture at the interface between the solder ball of ball grid array

package and conducting pads of PCB[2, 7, 8]. The corrosion of Ni-P alloy substrate is affected by process operating parameters such as pH value, temperature and phosphor concentration, *etc*. According to the previous reports [1, 2, 9], the pH value of the gold bath could have a great influence on the electrode potential, the deposition rate, and the surface morphologies. So it is necessary to study the immersion gold process and the Ni-P substrate corrosion during the gold deposition process at different pH values.

In this paper, we chose the pH as the most influential parameter among adjustable operation parameters in a non-cyanide sulfite and thiosulfate gold bath and investigated its effect on the immersion gold process. Thus, the effects of pH on the deposition rate, the coating structures, morphologies and open circuit potential was thoroughly investigated. The study was performed by measuring the electrode potential-time curves in situ and electrochemical impedance spectroscopy (EIS) in combination with X-ray fluorescence spectrometry (XRF) and atomic force microscopy (AFM) surface analysis.

2. EXPERIMENTAL

Copper samples with dimension of 20 mm×20 mm×0.25 mm, were used as electroless nickel plating substrate. These samples were prepared by treating the substrate with a series of pretreatment steps before electroless nickel and displacement gold deposition. Thus, they were first degreased in an acid cleaner for 5 min and then etched in a mixed solution of 100 g L^{-1} $Na_2S_2O_3$ and 10% H_2SO_4 for 1 min. After that they were dipped in 5% H_2SO_4 for 2 min. In order to activate the samples for subsequent EN plating, they were immersed in 30 mg L^{-1} $PdSO_4$ and 30 ml L^{-1} H_2SO_4 for 3 min. Then EN plating was performed in the EN bath with pH 4.8 for 10 min at 85°C, where 27 g L^{-1} $NiSO_4 \cdot H_2O$, 29 g L^{-1} $NaH_2PO_2 \cdot H_2O$, 25 ml L^{-1} lactic acid, and 12 ml L^{-1} malic acid were the main ingredients. After being rinsed in deionized water, the samples were immersed in the immersion gold bath for plating gold coating at 80 °C, where 2 g L^{-1} $Na_3Au(SO_3)_2$, 40 g L^{-1} Na_2SO_3, 15 g L^{-1} NaS_2SO_3, and 10 g L^{-1} $Na_2B_4O_7 \cdot 10H_2O$ were contained.

XRF (Brukeraxs S4 Explorer, Germany) was performed to confirm gold deposit thickness and the deposition rate at different pH values. The XRF spectra were evaluated by the automatic analysis program Spectraplus, and the gold thickness was calculated using MLQuantG software. The surface morphology of the coatings was examined by AFM (Molecule Imaging, Inc., USA). The AFM images were taken from four samples that were immersed in the gold deposition solution with different pH values.

For open circuit potential measurements, the Cu substrates were first sealed using insulated adhesive tape, except for a 2×2 cm effective working area, then coated by an EN layer. After thoroughly rinsing in deionized water, the specimens were immediately dipped into gold solutions as working electrodes for the open potential-time curves measurements. Open circuit potential was recorded as a function of time in a cell with two electrodes, a working electrode, and a reference electrode, using a CHI electrochemical station (model 660E). A Luggin capillary was placed near the working electrode to minimize the solution resistance. The counter electrode is a platinum plate, and

the reference electrode was a mercury sulfate electrode. All potentials were determined with respect to this reference electrode and were controlled by a conventional potentiostat with a programmer.

3. RESULTS AND DISCUSSION

3.1 Open circuit potential-time curves

Fig. 1 shows the electroless Ni-P alloy open circuit potential-time curves during the immersion gold process in a sulfite-thiosulfate solution with different pH values.

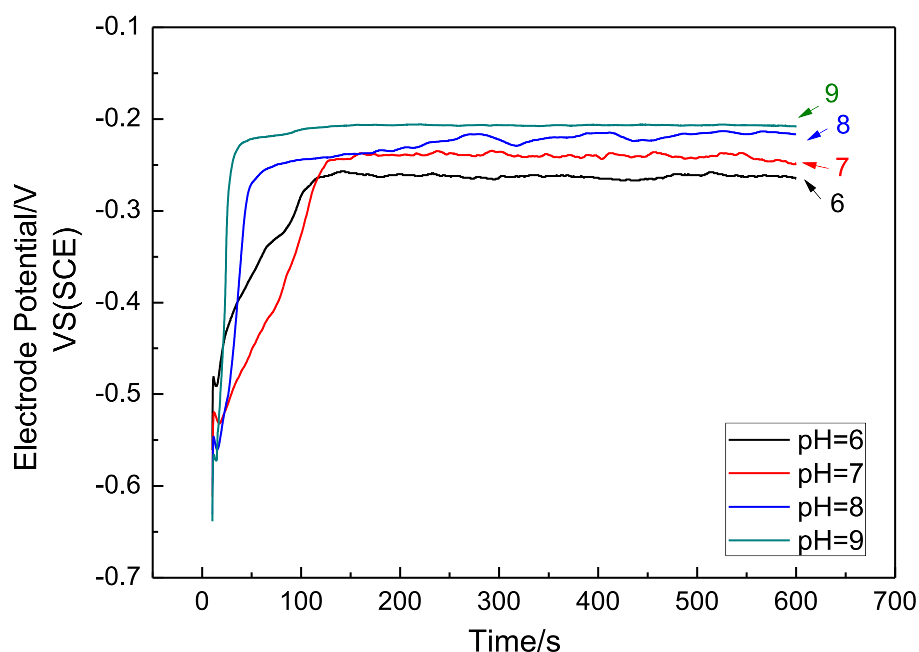


Figure 1. Dependence of open circuit potential-time curves on pH for immersion gold

Based on the characteristics of the curves, all the open circuit potential-time curves can be divided into two distinct phases: (1) at first stage, the potential positive shifts, (2) at second stage, the potential attains the steady plateau potential. In addition, according to Fig.1, with decreasing the solution pH from 9 to 6, the time for the potential to reach the plateau value becomes shorter and the plateau potential shifts to the negative direction. For example, at pH=9, the plateau potential is about -0.206 V, while at pH=6, the plateau potential is about -0.266 V. Thus, the plateau potential shifts to the negative for about 60 mV.

The gold-plating solution uses thiosulfate and sulfite as the mixed ligand, and no other reducing agent was contained. According to the basic mechanism of immersion gold plating on Ni-P alloy substrate, the process could be expressed as the following:

$$Au^{+} + Ni \rightarrow Au + Ni^{2+} \quad (1)$$

Moreover, it was reported that the gold deposition in the above solution is a substrate-catalyzed [10-12]. It was considered possible that either thiosulfate or sulfite (or both) could serve as the

reducing agent(s) in this substrate-catalyzed reaction. This deposition process can be expressed as the following:

$$2Au^{+}+SO_3^{2-}+H_2O \rightarrow 2Au\downarrow +SO_4^{2-}+2H^{+} \quad (2)$$

Thus, the displacement reaction and substrate-catalyzed reaction are both take placed in thiosulfate-sulfite mixed ligand system. Also, the latter reaction accounts for about 80% of the total deposit thichness[11, 12].

According to reaction (2), the potential of gold deposit [E(Au^{+}/Au)] could be described as follows by the Nernst equation

$$E_{(Au^{+}/Au)} = E^{0}_{(Au^{+}/Au)} - \frac{RT}{nF}\ln\frac{[Au]^{2}[SO_4^{2-}][H^{+}]^{2}}{[Au^{+}]^{2}[SO_3^{2-}]} \quad (3)$$

Since the initial pH value of the gold bath is for about 9, the low pH values such as 8, 7 and 6 were obtained by gradually adding appropriate amount of sulfuric acid. Therefore, the H^{+} concentration is increased as the pH value decreasing for 9 to 6. According to Eq. (3), a higher H^{+} concentration could decrease the $E_{(Au+/Au)}$, which indicates that the plateau potential of immersion gold decreases accordingly.

3.2 Immersion Gold deposition rate-time curves

The deposition rate-time curves of gold layer in the gold bath with different pH were analyzed by XRF analysis (shown in Fig.2). As can be seen from Fig. 2, the variation of deposition rate with time is similar. The initial deposition rate often has a higher value, and then deposition rate decreases with time. In addition, a higher deposition rate is often obtained at a lower pH value, indicating that at a low pH value the corrosion rate of underlying Ni-P alloy is also fast.

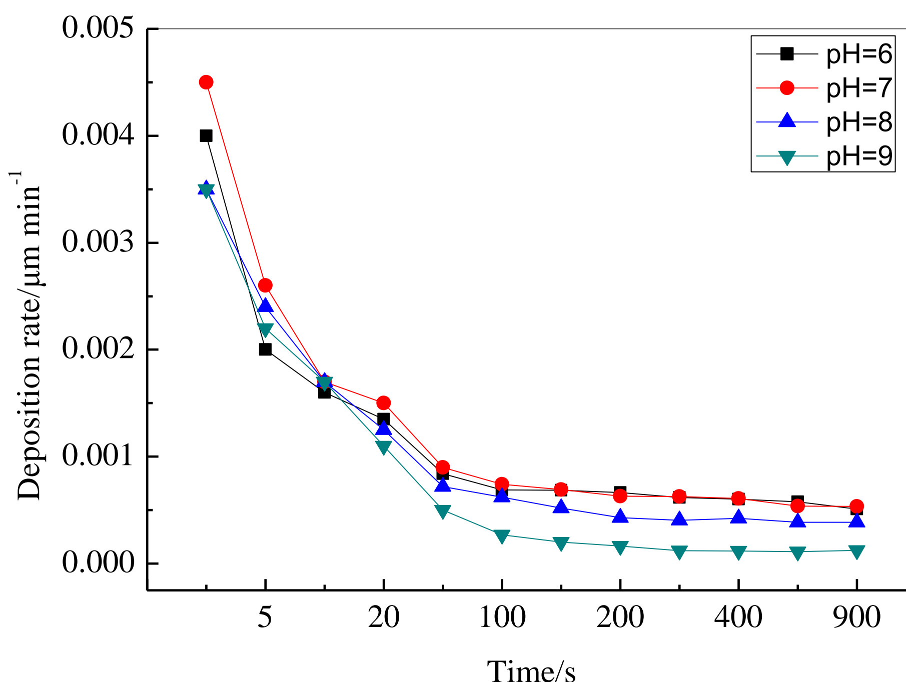
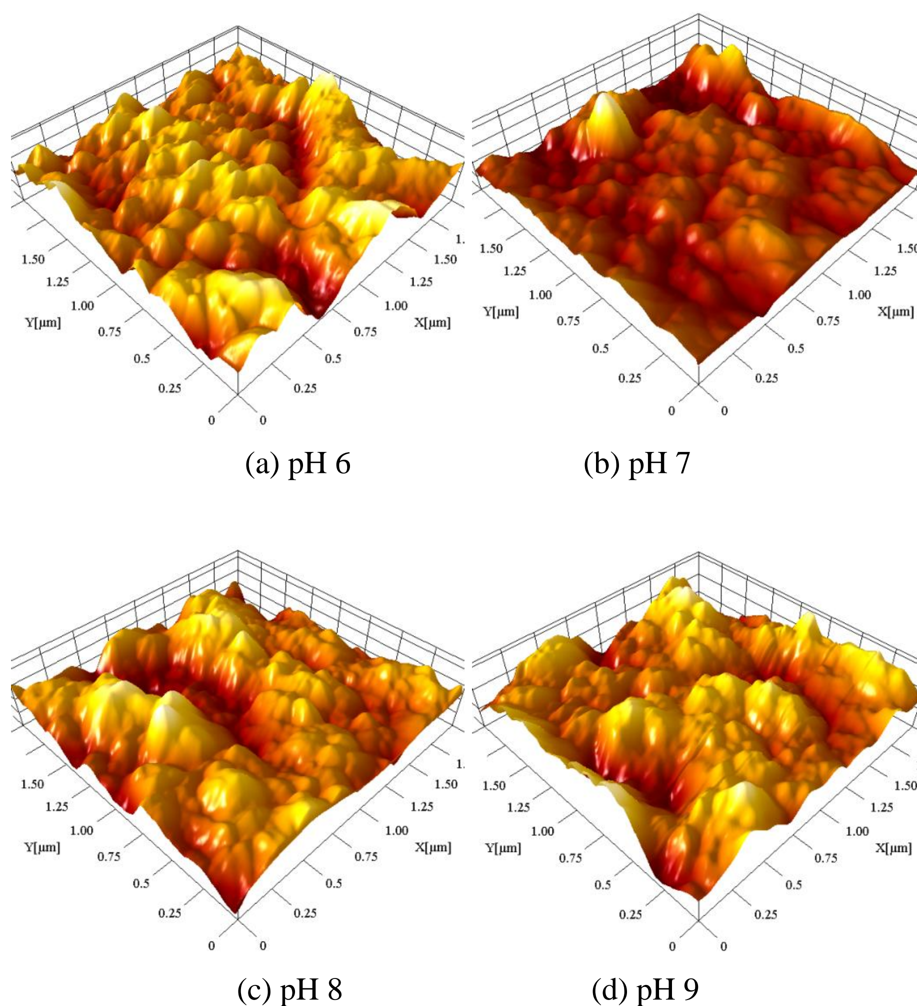


Figure 2. Dependence of deposition rate-time curves on pH for immersion gold

It's noted that the changes in electrode potential and deposition rate during the immersion gold process are related to the variation of the electrode surface state[1]. As electroless Ni-P alloy electrode begins dipping into the gold plating solution, in the EN surface, the Au^+-Ni galvanic cell is formed. Thus, Ni atoms oxidize, Au^+ reduces and deposits on the EN surface, and the deposition rate arrives the fastest. As the gold deposition proceeds, the nickel surface is gradually displaced by the gold deposit, accompanied with a positive shifting of the potential and a decrease of the deposition rate. As the deposition time is prolonged, a gold film is coated on Ni-P alloy substrate, and the electrode potential reaches the plateau value with a low deposition rate.

3.3 Immersion Gold Surface image

In order to confirm the effects of pH on immersion gold layer, we contrasted the surface of gold layers obtained from various gold baths. The surface of gold layer obtained from a low pH value gold bath (pH=5) has a yellow appearance with slightly black, while the gold layers obtained from higher pH value (such as 6, 7, 8) display a uniform golden yellow.



(a) pH 6 (b) pH 7

(c) pH 8 (d) pH 9

Figure 3. AFM morphologies of gold coating on Ni-P alloy substrates with phosphorous content of 9% at different pH

The AFM morphologies of the gold layers obtained at different pH value are shown in Fig. 3. The surface roughness of gold coatings is analyzed by SPIP software and presented in Table 1. According to Fig.3, all the gold coatings obtained at different pH value exhibit visible nodular structure, which is similar to our previous study[1].

Table 1. the Surface roughness parameters of gold coating deposited on Ni-P substrates at different pH

pH	R_a/μm	R_y/μm
6	15.4	74.3
7	9.92	40.7
8	5.69	28.7
9	4.61	27.5

The parameter of R_a (in Table 1) shows the arithmetic mean value of the gold layer height while R_y presents the distance between the peak and the valley of the gold layer surface. According to Table 1, as the pH increases, it is clearly observed that R_a and R_y decrease, indicating that the gold coating obtained in a bath with a high pH value often has a low roughness. These results are consisted with the change of deposition rate at different pH value. Thus, a higher deposition rate at a low pH value often leads to a higher gold film roughness.

Based on the results of 3.1-3.3, , for both the open circuit potential and the deposition-rate measurements during the immersion process, the results show significant changes in plateau potential and the deposition rate under different pH value. These changes reflect information originating from the gold-film formation and deposition process.

4. CONCLUSIONS

The results show that the deposition rate and electrode potential are changed during the immersion gold process. Both the mixed potential and the deposition rate have significant changes during the gold deposition process, indicating the variation of the electrode surface state. The open circuit potential, deposition rate and surface roughness are changed with pH value of gold solution. In the sulfite- thiosulfate gold solution, a higher pH value often means a positive electrode potential and a low deposition rate, and also a low gold layer roughness, which is conducive to obtain a good gold layer on Ni-P alloy substrate.

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