Korean J. Chem. Eng., **24**(6), 960-964 (2007)

Electrodeposition of palladium on the copper lead frame: Electrode reaction characteristics and the effects of primary additives

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(*Received 19 January 2007 • accepted 1 April 2007*)

Abstract−This study is mainly concerned with the electrodeposition of palladium on the copper alloy lead frame used for semiconductor assembly process. The role and effect of additives on palladium electrodeposition were studied by using various electrochemical methods. Ortho-formylbenzenesulfonic acid as a primary additive was used in palladium plating on the lead frame in this study. The electrochemical characteristics of electrode reaction were measured by the hanging mercury drop electrode for electrochemical system and the qualities of the plated surface of lead frames were also examined. The additive agent in Pd solution could have been classified as the grain refiner. It acted as the electroactive species, which increased the polarization and decreased the roughness, by adsorption on the electrode in palladium pre-plated process. The reduction of palladium ion was identified to be an irreversible reaction and the diffusion coefficient of palladium ion and the reaction rate constant were obtained from chronopotentiometry experiment.

Key words: Palladium, Electrodeposition, Lead Frame, Additives, Electrochemistry

INTRODUCTION

Recently, palladium (Pd) has been used instead of silver in the electroplating of lead frame for semiconductor packaging [1] due to many advantages such as the possibility of in-line assembly and the elimination of tin-lead alloy plating in semiconductor packaging processes. Assembly properties of wire bonderability, solderability and molderability crucially depend on the qualities of palladium pre-plated frame (PPF) for semiconductors [2]. Pd-PPF has been the focus of many investigations for its quality improvement, especially in plating solution and its additive agents. In plating solution even small amount of organic additives greatly affects the qualities of electrodeposited metal such as surface morphologies, texture, grain size and roughness [3]. In this respect, it is important to understand the role and effect of additives in palladium electrodeposition of PPF for semiconductors.

In electrodeposition, the qualities depend on various conditions that are the concentration of metal ion, cathodic current density, temperature, colloidal existence, agitation and so on, which affect the overpotential during the deposition of metal. Reported studies indicate that electrolyte essentially has low concentration of target metal ions which should be presented with the formation of atomic group between palladium ions and additives to gain good qualities in electrodeposition [3]. Thus more additives were added in the plating solution with high concentration of metal ions to create the fine grains on the surface in order to operate with high current density. It is widely known [4,5] that the formula of additives in plating solution for palladium is composed of sulfur-containing organic acids and their salts. Nevertheless, it is still unclear how the addition agents affect the electrodeposition of palladium ion because it is very difficult to measure and analyze the amount and composition of the additives in plating solution.

The present work is concerned with the primary additive effects on the electrodeposition mechanism and the surface qualities of palladium formed on the copper lead frame. For this purpose, ortho-formylbenzenesulfonic acid (OFB) is selected as an additive for palladium plating. According to the work [5], it has the structure of sulfur-containing organic acids and has comparatively better brightening effect on electrodeposited palladium. Cyclic voltammetry was applied for measuring the electrochemical characteristics by changing the amount of additive and AFM was used for the observation of the surface state of electrodeposited metal.

EXPERIMENTAL

1. Electrodepositon of Palladium on Copper Lead Frame

Palladium plating solutions were prepared by adding the various proposed amounts of additives. The experiments were performed based on the qualified Pd-PPF procedure and conditions. After the electrodeposition was carried out in the solution with 1.0 g/L OFB, the surface morphologies and roughness were measured. The electrodeposition and measurement of Pd layers were carried out over again for various amounts of OFB. All depositions were performed under Pd-PPF procedure and Table 1 shows the procedure of Pd-

Table 1. PPF procedure and condition employed

Process	Condition	Thickness
Electrocleaning	60 °C/10ASD/30 s	Base material
Activation	25 °C/20 s	-
Ni plating	55 °C/6ASD	40 μm inch (1 μm)
Pd plating	40 °C/2ASD	4-20 μm inch (0.1-0.5 μm)

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PPF preparation for copper lead frame and its thickness.

In this work the deposition of palladium on copper lead frame was carried out at a constant current density of 2 amperes per square decimeter (ASD). Samples with 1 cm^2 area were plated in a 1-liter glass jar with a magnetic stirrer. In this cell, both cathode and anode were placed vertically. The solution for the deposition of palladium was operated at 40 °C and pH 7. Palladium-deposited surfaces were observed in air by means of AFM with Park Scientific Instrument Co. About five images of different areas were analyzed on each sample in order to get the average roughness value. All images were 5×5 μm square in size, digitized in 400×400 pixels and obtained with a scanning frequency of about 1.04 Hz. Surface roughness was quantified by its RMS value.

2. Electrochemical Measurements

The electrochemical characteristics of palladium plating solution with various amounts of OFB were measured as follows. First, a solution without OFB was used for the determination of its electrochemical characteristics, and a solution with OFB was tested by the same methods. The cyclic voltammetry, chronopotentiometry and differential pulse polarography were carried out in order to identify the relations between the amount of OFB and size of peak current densities. The electrochemical measurements were performed with a polarographic analyzer interfaced directly to a mercury drop electrode with an active working surface of 0.95 mm^2. Platinum wire was used as a counter electrode, and an SCE as a reference electrode. All electrochemical experiments were performed at 21.0± 0.2 °C. The 0.1 M ammonium sulfate buffers were used as supporting electrolytes. Before measurements were made, each solution was purged with nitrogen for 10 min. A nitrogen "blanket" was also blown over the solution surface at all times. Table 2 gives formulas for the palladium ammonium bath used in this study. The voltammetric experiments were carried out with an EG&G PARC Model 273A potentiostat/galvanostat, equipped with a 303A hanging mercury drop electrode and connected to a computer through an IEEE-488 interface.

RESULTS AND DISCUSSION

1. Palladium Plated Surface

Fig. 1 shows the morphologies of palladium on the copper lead frame to be plated by Pd-PPF process with the proposed amounts of OFB in its plating solution. Considerable differences can be seen in the grain morphology observed from the deposition images. Especially, Fig. 1(a) shows Pd-PPF electrodeposited in solution without OFB.

The grain size on lead frame plated in solution without OFB (a) was coarser than the others. It was observed in these images that with the increase of OFB amounts grains became finer in size. The addition of OFB gave rise to the decrease of the roughness on deposited surface. The roughness became clearly different in much thicker Pd layers. It becomes very strongly increased when the thickness is larger than 0.3 μm deposited on copper lead frame in bath solution without OFB. But the others plated in solutions with OFB show little difference regardless of deposited metal thickness or its OFB amount as shown in Fig. 2. From the viewpoint of roughness of surface, the optimum thickness was the 0.2 μm when plated in bath with 0.5 g/L OFB.

Fig. 3 shows the thickness histograms and Table 3 shows the values of average and deviation of palladium layer deposited on lead frame at the same condition with the exception of the amount of additive. The proposed thickness for palladium plating condition was set as 0.3 μm. Adding the OFB 0.5 g/L as primary addition agent in bath caused the thickness deviation to decrease from 0.03697

Table 2. Composition of Pd ammonium bath

Class	Reagent	Amount
Pd metal source	$[Pd(NH_3)_4]_2Cl_3$	5 g/Las Pd
Conductive	$(NH_4)_2SO_4$ or NH_4Cl	50 g/L
Stabilizer	Na_2-EDTA	2-35 g/L
Buffer	K_2HPO_4	-

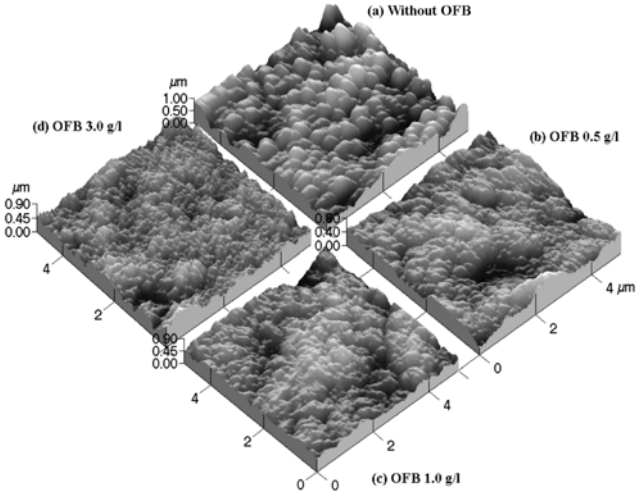

Fig. 1. Three-dimensional AFM images of the palladium surface plated in palladium ammonium bath containing different amounts of OFB at applied current density of 2ASD.

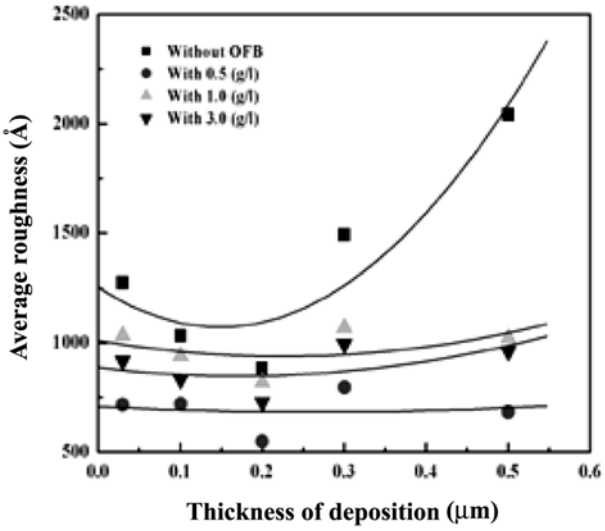

Fig. 2. Roughness of the electrodeposited surfaces plated with various OFB amounts in Pd ammonium bath measured by AFM.

(A) to 0.02610 (B). Both the average and deviation of thickness were remarkably decreased by adding OFB more than 0.5 g/L, which led average plated thickness to go down to 0.1 μm than expected value. As 3.0 g/L OFB, which is much more excessive in electroplating bath, was added in solution, Pd film grew less and the thickness became the lowest one than the other cases. It was found that the amount of OFB affects the growth and creation of palladium seeds on lead frame. It could be identified as a refiner in Pd electrodeposition [3].

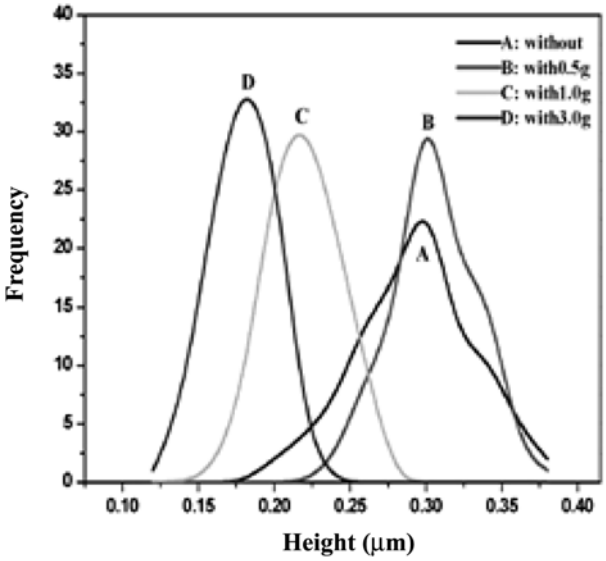

Fig. 3. Thickness histograms of electrodeposited Pd layers with various OFB amounts at the same applied current density and deposition time.

Table 3. Thickness of deposited palladium

OFB amount	Average (μm)	Standard deviation
Without	0.293	0.03697
0.5 g/L	0.306	0.02610
1.0 g/L	0.220	0.02177
3.0 g/L	0.180	0.01976

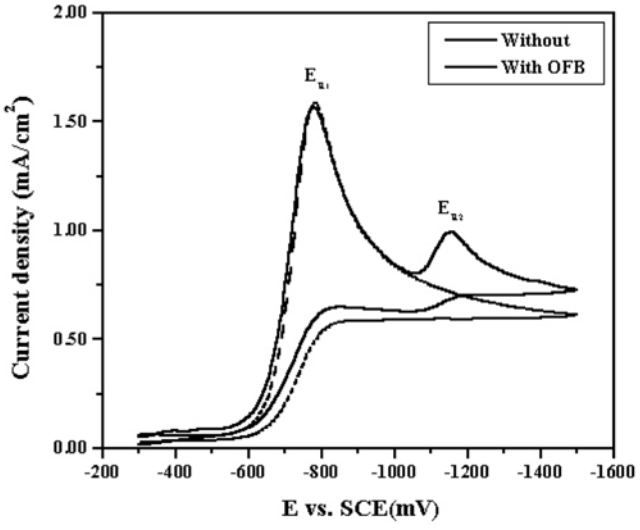

Fig. 4. Cyclic voltammograms obtained with sweep rate of 50 mV/s for hanging mercury drop electrode as working electrode after addition of various amounts of OFB to palladium ammonium baths at 25 °C and at pH 7.0.

2. Electroactive Species in Pd Plating Solution

Electrochemical characteristics were measured by potential sweep technique, which can be normally used to diagnose mechanisms of electrode reactions, for the identification of species present in solution and for semi-quantitative analysis of reaction rates [5]. Fig. 4 shows the responses of cyclic voltammetry for palladium ammonium bath with and without OFB in which both reactions were irreversible. It was found that there was one electroactive species in palladium bath without OFB, because just one peak was detected in the voltammograms. The peak potential (E_p) was −0.812 V vs. SCE. This electrode reaction is the reduction of palladium ion as in the following equation [6].

$$[Pd(NH_3)_4]^{2+}+2e^- \rightarrow Pd,\ E_0=-0.756\ V(SCE) \quad (1)$$

On the other hand, another peak was detected between the reduction of palladium and evolution of hydrogen in bath with OFB of 1.0 g/L and the peak potential (E_p) was −1.184 V vs. SCE in cathodic direction. The peak potential (E_p) and peak current (i_p) were measured by increasing the amount of additive in palladium ammonium bath to check the OFB as an electroactive species in the bath by differential pulse polarography.

Fig. 5 shows responses of differential pulse polarography by OFB added. The peak current density increased at the same reduction potential in proportion to the amount of OFB added in the bath. Where the peak potential is −1.180 V vs. SCE, the relation between the peak current density and the amount of OFB in the bath is 2.85 ASD/g/L. Consequently, it was observed that there are two kinds of electroactive species, which are palladium ion and OFB, and it was calculated that their half wave potential ($E_{1/2}$) was −0.724 V vs. SCE and −1.114 V vs. SCE, respectively, at 25 °C and at pH 7.

3. Electrode Reaction

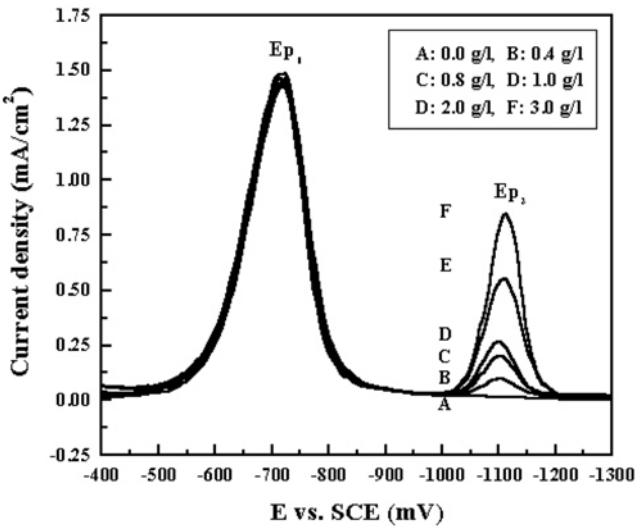

Fig. 5. Analysis of OFB agents in palladium ammonium baths by using differential pulse polarography obtained with sweep rate of 10 mV/s, scan height of 50 mV and at pH 7.0.

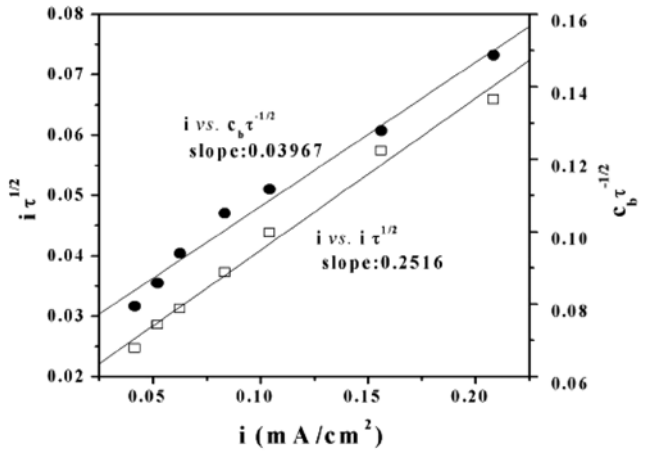

Fig. 6. Diagnostic plots of the reduction of palladium ion measured by constant current chronopotentiometry.

Fig. 6 shows the diagnostic plots of reduction of palladium ion measured by constant current chronopotentiometry. It was found that the reduction of palladium ion is a mass transfer controlled reaction that is affected by the diffusion of metal ions due to the increase of concentration in the transition time (τ).

An increment in the applied current caused the transition time (τ) to decrease at the constant concentration as shown in plot of $\tau^{1/2}$ vs. applied current, that is, the potential became higher in the cathodic direction in proportion to the applied current. It was described that the palladium ionic concentration is reduced on the electrode due to their reduction reaction and so the reduction potential is expected to be much higher in cathodic direction in order to maintain their electrode reaction [5]. Therefore, the electrode potential moves to the cathodic direction. The diffusion coefficient of palladium ion, D_o, 2.1×10^{-8} cm^2/s, could be determined with the measured value of τ at the known value of current density (i), of which $i\sigma^{1/2}$ was obtained at various current densities, given by Sand equation.

$$2i\tau^{1/2}=nFA\,C_o^*\,D_o^{1/2}\pi^{1/2} \quad (2)$$

Where, C_o^* is initial concentration, τ is transition time, i is applied current density.

The reduction of palladium ion in bath is an irreversible reaction; therefore, the peak current density represents the following equation, known as the Randles-Sevick equation.

$$i_p=(2.69\times10^5)n(\alpha n_a)^{1/2}\,A\,D_o^{1/2}\nu^{1/2}C_o^* \quad (3)$$

Table 4. Reduction of palladium ion measured by linear sweep voltammetry

Sweep rate	Solution without OFB		With OFB	
υ (mV/s)	E_p (V)	i_p (mA/cm^2)	E_p (V)	i_p (mA/cm^2)
10	0.760	0.88	0.760	0.90
20	0.770	1.19	0.765	0.17
50	0.780	1.82	0.775	1.76
100	0.790	2.49	0.785	2.45
150	0.795	3.04	0.790	2.98
200	0.780	3.49	0.795	3.44

Linear sweep voltammetry was carried out with various sweep rates (υ) to determine the rate constant of palladium ion reduction reaction.

Table 4 shows the measurement values of the peak current (i_p) and its potential (E_p) with various scan rates.

$$i_p=0.227\times10^{-3}nFAk^0\exp[-(\alpha n_aF/RT)(E_p-E_0)] \quad (4)$$

where k^0 is standard heterogeneous rate constant.

The rate constants (k^0), 3.617×10^{-1} cm/s could be determined from the plots of log i_p vs. E_p and Eq. (4) derived by Randles-Sevick. Since the peak current density at irreversible reaction is proportional to the amount of palladium ions and the scan rate, the rate constant can be obtained from known values of the electrode reaction such as the number of electrons (n), diffusion coefficient (D_o) and electrode area (A). At these results, a peak potential (E_p) that is a function of a sweep rate in an irreversible reaction has an inclination to shift to the negative direction by 30 mV for a tenfold increase of u. E_p occurs beyond E^0 due to an activation overpotential related to k^0. And the rate constant decreases to 3.09×10^{-1} cm/s by addition of OFB in palladium bath.

Fig. 7 shows responses of cyclic voltammetry with copper lead frame in the same palladium solution for electrochemical measurement. In Fig. 7, reduction of palladium at copper lead frame seems to be an irreversible reaction. There is just one peak potential in all experimental results with lead frame. The broad peak potential is –0.774 V in cathodic region in solution without OFB. The highest curve in the dashed line was observed by the addition of 1.0 g/L OFB in solution. The peak potential shifts to the negative direction by 0.110 V. But the cathodic peak current density increases from 1.34 mA/cm^2 to 1.52 mA/cm^2. The peak current density becomes higher in solution with OFB than that in solution without OFB.

Fig. 8 shows that the rest potential tends to move toward the negative direction by the addition of OFB in Pd solution. Until the addition of 1.0 g/L OFB, the curves move to cathodic direction when

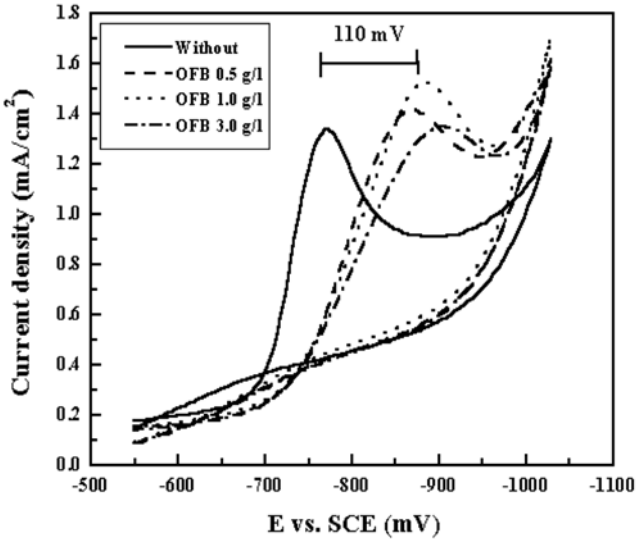

Fig. 7. Cyclic voltammograms with sweep rate of 50 mV/s for a copper alloyed electrode as working electrode in palladium ammonium baths containing various concentrations of OFB agents at 25 °C and at pH 7.05.

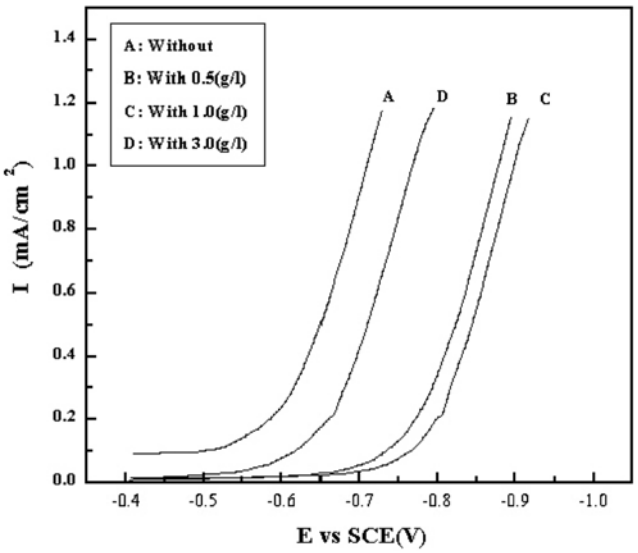

Fig. 8. Linear polarization curves of Pd ion reduction with various OFB amounts in palladium ammonium baths.

increasing the OFB amount. The cathodic polarization curves were influenced by OFB due to its adsorption effect. But the addition of 3.0 g/L OFB in Pd solution, which is a very excessive amount in bath, causes the rest potential to shift to anodic direction. It can be expected that the excess of OFB may inhibit the Pd ion reduction reaction due to the strong coverage of OFB on the surface of electrode. This phenomenon should be investigated in more detail; however, this large excess amount of OFB cannot be applied in practical use.

CONCLUSIONS

The role of OFB additive in palladium ammonium bath for plating in Pd-PPF was found as grain refiner increasing the cathodic polarization by carrying out the electrochemical investigation within our experimental ranges of OFB amounts. There are two kinds of electroactive species in this solution--palladium ion and OFB--which is quantitatively analyzed by differential pulse polarography, and which affects the reduction rate of the palladium ion and the creation of their seeds on lead frame.

The deposited palladium roughness on lead frame is clearly seen to decrease due to the addition of OFB in this process, but the effect is not proportional to its amount. The optimum condition is obtained from experimental results related to the values of roughness, peak current and peak potential. Considering all experimental results obtained in this work, the amount of OFB as a refiner in Pd electrodeposition should be set below 1.0 g/L.

ACKNOWLEDGMENT

This study was supported by Samsung Techwin Co. and Hongik University (03) research funds.

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