Thick pure palladium film with varied crystal structure electroless deposited from choline chloride–palladium chloride solution without the addition of reductant

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ABSTRACT

Immersion deposition procedure was applied to achieve thick pure palladium films with thickness up to about 3 μm from choline chloride (ChCl)–palladium chloride (PdCl$_2$) aqueous solution without addition of reductant at 60 °C. Using X-ray diffraction and scanning electron microscope, it was confirmed that Pd films with different crystal orientations and morphology were obtained just by varying the immersion time, and Pd (111) crystal orientation predominated over other crystal orientations during the initial deposition procedure, while (220) conquered (111) about 45 min later. ChCl performing as a reductant facilitated the growth of thick Pd film free of reductant. The immersion deposition of Pd followed the mechanism of replacement reaction accompanying with autocatalyzed reaction and autocatalyzed reaction predominating over replacement reaction. The results revealed that Pd films prepared from ChCl–PdCl$_2$ solution had excellent properties on solderability and corrosion resistance.

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1. Introduction

Palladium (Pd) is an important platinum group metal for various technologies including catalysis [1], sensors [2] and contact material for electric components [3]. The fabrication of Pd related materials, such as Pd films or membranes, could be achieved mainly by electroplating [4,5] and electroless plating [6–8]. Due to the attractive merits including low cost, simple equipment, ability to deposit on conductive and nonconductive surfaces with complex shapes, electroless plating is generally preferred. There are two kinds of electroless deposition techniques. One is autocatalytic procedure, which is promoted by the redox reaction between a metal ion complex and a reductant. The other is immersion procedure, which is characterized as galvanic replacement of a based active metal by a relatively inactive metal ion.

To get thick electroless Pd films, sodium hypophosphite was often added to the plating solutions as reductant to allow metal deposition and increase the thickness continually during the deposition process, however, the achieved films were not pure Pd but Pd–P alloy [6,9–11]. Dogan et al. [12] presented composite Pd membrane synthesis on porous glass supports using the electroless deposition technique with hydrazine as reductant. However, the stability of electroless plating solutions decreased with the presence of reductant. Thus, some ligands, such as ethylenediaminetetraacetic acid (EDTA) [6] or disodium EDTA [12], triethyleneamine [6] and ammonia [10], which are not so environment friendly, are always introduced to stabilize the plating solutions.

Choline chloride (2-hydroxyethyltrimethylammonium chloride, HOCH$_2$CH$_2$N(CH$_3$)$_3$Cl, ChCl) as a quaternary ammonium salt is widely applied to metal [13] and alloy electrodeposition [14–20] in the form of deep eutectic solvents (DESs). Böck et al. [21] electrodeposited Pd on copper rods from ChCl/urea/PdCl$_2$ solution by direct and pulse current modes. Hammons et al. [22] fabricated Pd nanoparticles on glassy carbon surface by electrodeposition from ChCl/urea solution. However, relatively lower attention was paid to metal electroless deposition from ChCl based DESs [23,24]. Recently, we applied ChCl, which served both as solvent and ligand, to perform sustained electroless silver (Ag) [25] and tin (Sn) [26] deposition in ChCl–H$_2$O solutions, and the plating solutions for Ag and Sn deposition were very simple and stable. Vreese et al. [27] also reported that crystals of CuCl$_2$·2H$_2$O, Cu(choline)Cl$_3$, [choline]$_4$[Cu$_4$Cl$_{10}$O] and [choline]$_3$[CuCl$_4$][Cl] were formed in the ionic liquid ChCl–CuCl$_2$·2H$_2$O, which indicated that ChCl performed as ligand. From what have been discussed above, it has the possibility to apply ChCl to perform electroless Pd deposition. Nevertheless, to date, applying ChCl to electroless Pd deposition has not been published.

In the present work, thick pure Pd films were obtained from ChCl containing solution by immersion deposition without addition of

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reductant. Pd films with different crystal orientations correspondingly varying with immersion time were investigated by energy dispersive X-ray spectroscopy (EDX), optical microscope, scanning electron microscope (SEM) and X-ray diffraction (XRD). The mechanism of Pd deposition procedure was also deduced.

2. Experimental details

2.1. Materials and methods

Ni–P coated Cu sheets ($50 \times 20 \times 0.3$ mm, Anhui Jingcheng Copper Co. Ltd., China) were used as the substrates for Pd deposition. All solutions were prepared with analytical grade reagents and distilled water.

The procedure of electroless Pd deposition is briefly as follows: Before electroless plating, the Cu sheets were degreased with basis solution and micro-etched in acid solution, then activated in activating solution (0.1 g L^{-1} PdCl$_2$ and 10 mL L^{-1} HCl) at 30 °C for 1 min. After each of these pre-treatment steps, the substrates were rinsed with distilled water and dried under air flow. Then, the sheets were immersed into the electroless Ni plating solution (25 g L^{-1} NiSO$_4$·6H$_2$O, 30 g L^{-1} NaH$_2$PO$_2$·H$_2$O, 30 g L^{-1} sodium citrate, 20 g L^{-1} CH$_3$COONa, pH 4.5, 80 °C, 40 min) to perform electroless Ni deposition. Ni–P films with the thickness of about 3.5–4.0 µm were obtained for the following electroless Pd deposition. Finally, the Ni–P plated Cu sheets were immersed in the Pd plating solution for desired immersion time to perform electroless Pd deposition. The compositions and operating conditions of the Pd plating solution are listed in Table 1. During the electroless procedures, the plating solutions were agitated using rotating magnetic and the stirring speed was 500 rpm.

2.2. Characterization of films

The deposition rate was defined as increased thickness of as-plated films in unit time (µm h^{-1}). Considering the limitation of EDX and the precision of the optical microscope, Pd film deposited on Cu/Ni–P surface with the thickness under 1 µm was measured by EDX (EDX1800, Skyray Instrument Co. Ltd., China), and the thickness of above 1 µm was measured by optical microscope (JSM-6360L, Japan Electron Optics Laboratory Co. Ltd., Japan, ×1000) viewing the cross-section of Pd coated plates. For EDX detection, every sample was tested for 9 random points, and every point replicated for 3 times, the thickness is the average results of 9 points. While, for optical microscope viewing, the thickness is the average results of 20 random points.

Structure and morphology of Pd films were investigated by XRD (Rigaku D/max 2500 powder diffractometer, Cu Kα ($\lambda = 1.542$°A) radiation at 30 kV and 40 mA, scan rate at 6° min^{-1}, 2θ from 30° to 90°) and SEM (JSM-6360LA, Japan Electron Optics Laboratory Co. Ltd., Japan), respectively. In order to describe the structure and estimate quantitatively the preferred orientation of the Pd deposits, the relative texture coefficient (RTC$_{(hkl)}$) was calculated, which is defined as [28]:

$$RTC_{(hkl)} = \frac{I_{(hkl)}/I^0_{(hkl)}}{\sum_1^4 I_{(hkl)}/I^0_{(hkl)}} \times 100\% \qquad (1)$$

where I$_{(hkl)}$ are the diffraction intensities of the (hkl) lines measured in the diffractogram of the deposit and I$^0_{(hkl)}$ are the corresponding intensities of a standard Pd powder sample randomly oriented from JCPDS 46-1043. The summation in the denominator is taken for the four "basic" lines visible in the diffraction pattern, i.e. (111), (200), (220) and (311).

The concentrations of ions in plated solutions were detected by sequential plasma spectrometer (ICPS-7510, Shimadzu, Japan). During this experiment, the substrates were restricted to 1 cm^2.

Solderability of films was determined by a wetting balance using solderability tester (SKC-8H, Shanghai Runpu Inspection Equipment Co. Ltd., China). Sn63Pb37 was used as eutectic solder, and the liquid solder was kept at a constant temperature of 235 °C during tests [29].

Corrosion resistance was performed by potentiodynamic polarization technique on an electrochemical analyzer (RST-5200F, Suzhou Risetest Instrument Co. Ltd, Suzhou, China) in 3.5 wt.% NaCl solution. The counter and the reference electrodes were platinum wire electrode and saturated calomel electrode, respectively. For comparison, the working electrode was Ni–P/Pd coated and Ni–P coated Cu sheets. The area of working electrode exposed to solution was 1 cm^2 and the scan rate was 10 mV s^{-1}.

3. Results and discussion

3.1. Effects of plating parameters on Pd deposition

Here, we developed a simple immersion Pd plating solution containing only ChCl, PdCl$_2$, H$_2$O and pH adjuster. This section presents the results obtained from investigating the influences of the plating parameters, such as the concentration of ChCl and PdCl$_2$, pH value, and the plating temperature on the deposition rate. The optimal conditions were determined by the deposition rate and the brightness of Pd film. The relationships between the plating parameters and the deposition rate is shown in Fig. 1.

As is shown in Fig. 1(a), the deposition rate gradually decreased with the increase of ChCl concentration. There may be two reasons accounting for this phenomenon. On the one hand, the viscosity of ChCl–H$_2$O solution becomes higher with the increase in ChCl concentration. As a result, the migration ability of Pd^{2+} decreased, and Pd^{2+} was less likely to be reduced on the substrate surface resulting in the decline in the deposition rate. On the other hand, ChCl might perform as a ligand to form complex with Pd^{2+}. The supposition was verified by ultraviolet absorbance curves of PdCl$_2$ in ChCl–H$_2$O solutions showing an increasing absorbance with the increasing ChCl concentration at the wavelength of 279 nm. Coordination equilibrium between ChCl and Pd^{2+} is speculated. An increase in ChCl concentration let to a shift in equilibrium toward a decrease of free Pd^{2+} weakening the effective collision between Ni and Pd^{2+} in Pd deposition. During the experiments, the plating solution became unstable during the process of plating and the film appearance is white when ChCl concentration was lower than 20 g L^{-1}. However, the deposition rate was too slow and the film turned to dull and nonuniform appearance when ChCl concentration was higher than 60 g L^{-1}. Considering the deposition rate, appearance of Pd film and the stability of the plating solution, the optimum concentration of ChCl was chosen as 40 g L^{-1}.

As can been seen in Fig. 1(b), the deposition rate increased dramatically with the increase of PdCl$_2$ concentration. This could be explained that more and more free Pd^{2+} were presented in the solution with the increase of PdCl$_2$ concentration. Consequently, the speed of the reaction between Ni and Pd^{2+} promoted. During the experiments, Pd films presented dull appearance with PdCl$_2$ concentration higher than 2.5 g L^{-1}. Considering the deposition rate and the amount of PdCl$_2$, the optimum concentration of PdCl$_2$ was 2.0 g L^{-1}.

In this work, the effect of pH value was studied ranging from 0.6 to 2.0 using HCl solution as a pH adjuster. As is shown in Fig. 1(c), there was a slight decrease in the deposition rate with the increasing pH

Table 1
Composition and operating conditions for Pd deposition.

Chemicals	Basic concentration	Condition
PdCl$_2$ (g L^{-1})	2	–
ChCl (g L^{-1})	40	–
Temperature (°C)	–	60
pH (HCl)	–	1.0
Immersion time[a] (min)	–	Varied

[a] The immersion time in Section 3.1 was 5 min.