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Comparative study on physical and electrochemical characteristics of thin films deposited from electroless platinum plating baths

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ABSTRACT

Physical and electrochemical properties of deposits obtained from two types of electroless platinum plating bath were investigated. One bath contained hydrazine as the reducer and lead monoxide as the stabilizer (HYD bath), and the other contained sodium borohydride (SBH) as the reducer and sodium thiosulfate as the stabilizer (SBH bath). The deposit obtained from the SBH bath had a high electric resistivity (6.0×10^{-5} Ω cm), large tensile stress (421 MPa at 0.3 μm thickness) and rough surface ($R_a = 19.2$ nm) compared to HYD bath. Approximately 5 times more gas emission from the SBH bath was confirmed during electroless plating than HYD bath. The hydrogen emission during plating affected the physical properties of the resulting deposit and explained the rougher surface of platinum films from the SBH bath. The CV measurement using the deposits as the working electrode also correlated with surface area. Less than 0.5 wt% of sulfur inclusion deriving from the stabilizer into the SBH bath deposit did not affect the surface roughness or electrochemical properties.
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1. Introduction

Platinum has been widely applied in the various industrial fields often functioning as a catalyst. Due to its unique physical and chemical properties such as corrosion resistance, thermal stability and high catalytic activity for various chemical reactions, platinum has been applied in autocatalysis, fuel cells, and as an electrode material. However, platinum deposition control by electroless plating has proven difficult compared to other precious metals such as gold and palladium [1]. Therefore, there has been limited scientific literature available regarding electroless platinum plating baths and evaluation of deposited films. Metallization of polyethylene terephthalate by electroless platinum deposition technique has been studied for the purpose of implantable medical devices application [2]. In addition, platinum metallization of polymer materials has a potential ability of application to various sensor devices. In most studies on electroless platinum, hydrazine has been utilized as the reducer [3–5]. In contrast, only a few studies have been conducted related to electroless plating bath using sodium borohydride (SBH) as the reducer [6,7]. The stabilizing mechanism of sulfur–bearing additives in an electroless platinum plating bath with SBH as the reducer has been established along with an electrochemical method for selection of sulfur stabilizers [8]. However, physical and electrochemical characterization of deposited films still remains limited.

The plating bath composition and plating conditions influence the characteristics of the deposited films. Therefore clarification of the relationships between plating parameters and deposit characteristics is invaluable for effective selection of the plating bath most suited to the purpose of deposited film. Variables also arise due to the multiple chemical components of electroless plating baths which consist of at least five components; the metal ion source, complexing agents, reducer, stabilizer and pH adjuster. Of the bath components, the reducer and stabilizer often affect the structure and chemical composition of the deposit due to adsorption onto the deposit surface or co–deposition. Thus, it is fundamental importance to clarify the effect of the reducer and stabilizer on physical and morphological characteristics such as electric resistivity, internal stress, hardness and surface roughness of the deposits. In order to elucidate plating bath – deposit character correlations, comparison of reducers and stabilizers utilized in electroless platinum plating baths was performed. The deposits from a hydrazine reduced bath with lead as the stabilizer (HYD bath) and an SBH reduced bath stabilized by a sulfur additive (SBH bath) were characterized. Furthermore, the effect of gas emission from oxidation of reducers during the plating reaction was taken into consideration. In addition to platinum deposit characterization by tensile stress, X-ray diffraction (XRD), morphology and elemental composition analysis, the deposits were also electrochemically characterized using cyclic voltammetry. Correlations between the platinum plating bath and resulting deposit character

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should contribute to the expansion of application electroless plating in the relevant fields.

2. Experimental procedures

2.1. Electroless plating baths and plating process

The HYD and SBH bath compositions shown in Table 1 was designed based on previous studies [8,9]. The HYD bath was stable for 3 or 4 days and SBH bath up to 4 weeks when stored at room temperature, however all plating tests were conducted within a day from the time it was made up. The platinum salt ($Pt(NH_3)_6Cl_4$) was prepared from pure platinum powder (99.95% or more). The surface tension of the HYD and SBH plating baths were 7.2×10^{-4} N cm^{-1} and 7.4×10^{-4} N cm^{-1}, respectively. Both values were close to that of pure water (7.3×10^{-4} N cm^{-1}). Another plating bath, HYD_S bath, was examined in order to clarify the influence of reducer on deposit sulfur inclusion. The HYD_S bath had the same chemical composition as HYD bath except that 0.0062 mM of sodium thiosulfate was added as the stabilizer instead of lead monoxide. The HYD_S bath was operated at pH 11.0 and at 70 °C. An electrochemical analysis based on the mixed potential theory of the HYD and SBH baths is given in Appendix.

For copper substrate, copper sheets were pretreated by degreasing (50 °C, 4 min), chemical etching (30 °C, 1 min), acid rinsing (5 vol% H_2SO_4, 30 °C, 1 min) and platinum catalysis deposition (50 °C, 3 min). The platinum catalyzing solution consisted of 0.5 mM of H_2PtCl_6 and 2.4 M HCl from which platinum could be deposited on the substrate surface by displacement of copper. After the pretreatment, the substrates were plated by submersion in one of the plating baths. For gold substrate, the same pretreatment as copper was performed except the chemical etching and catalyzing steps were skipped. For cycloolefin polymer (COP) substrates, a UV modification method was adopted [10,11]. First, 100 μm thick COP (Zeon Co. Ltd. Zenor ZF-16) film was exposed to 6.4 mW cm^{-2} at 185 nm and 63 mW cm^{-2} at 254 nm irradiation from a low pressure mercury lamp (Koto Electric Co. Ltd. KOL1-300S) for 3 min. After exposure, the cleaved low molecular weight material was removed by treatment in 50 g dm^{-3} NaOH solution at 60 °C for 2 min to give a modified surface. Palladium catalyst was then adsorbed onto the modified surface by sequential submersion in a conditioning solution (Rohm and Haas CC231, 10 vol% aqueous solution, 2 min, 45 °C), catalyzing solution (2 min, 45 °C) and acceleration solution (2 min, 60 °C). The palladium catalyzing solution consisted of 0.3 g dm^{-3} of $PdCl_2$ and 0.3 vol% of concentrated HCl and the acceleration solution consisted of 1 g dm^{-3} of SBH and 10 g dm^{-3} of NaOH. Electroless platinum plating was then accomplished by submersion of the palladium catalyst adsorbed COP film in one of the electroless plating baths. Deposit thickness was controlled by immersion time, and was measured using an X–ray fluorescence (XRF) film thickness gauge (Hitachi High–Tech Science SFT9500).

2.2. Platinum deposit analysis and characterization

The surface morphology of the deposits was observed using scanning electron microscopy (SEM, JEOL JSM–7000F), and surface roughness of deposit on COP film was evaluated using atomic force microscopy (AFM, JEOL JSPM–4210). The XRD patterns from deposited platinum films were observed using an X–ray diffractometer (Rigaku RINT2000). As often studied, the grain size of the deposit was estimated from the width of the diffraction peaks using Scherrer's formula [12,13]. The content of lead or sulfur in the deposits was analyzed by dissolution in aqua regia (mixture of 20 vol% of nitric acid and 80 vol% of hydrochloric acid) and analysis of the solution by inductively coupled plasma atomic emission spectroscopy (ICP–AES, Shimadzu ICPE–9000).

Sheet resistance of the platinum deposited on COP film was measured using a resistivity processer (NPS Inc. Model sigma–5). Electrical resistivity of the deposit from each bath was estimated from the linearly proportional region (when $1/t$ was $<1 \times 10^5$ cm^{-1}) of the relationship between reciprocal thickness and sheet resistance;

$$\rho_S = \rho/t \quad (1)$$

where ρ_s is the sheet resistance, ρ is the electric resistivity and t is the thickness of the deposited film.

Internal stress of the deposited films was obtained from the curvature radius using Stoney's equation [14];

$$\sigma = \frac{Ed^2}{6rt} \quad (2)$$

where σ is the internal stress of the deposited film, E is the Young's modulus of the substrate, d is the thickness of the substrate, r is the radius of curvature and t is the thickness of the deposited film. This principle has been widely used to evaluate internal stress of plated films such as electroless nickel [15]. A forked test strip (Specialty Testing and Development Company Inc. copper alloy C194) and the deposit stress analyzer (Model 683EC) were used to estimate the radius of curvature r [16]. In order to submerse the test strip completely in the plating bath, 0.6 dm^3 of each plating bath was used under the condition described in Table 1. The plating process for copper was adopted except the chemical etching step was skipped to avoid excess damage to the resist on the test strip, and thickness of all the deposits was adjusted to 0.3 μm for the internal stress measurement.

Knoop hardness of the film deposited on copper sheet was estimated using a microhardness tester (Mitutoyo HM–221). The mean value of eight trials per sample was recorded.

2.3. Measurement of gas volume

A pretreated copper piece (25 × 20 mm) was placed in a syringe (Ohsaka Chemical Co., Ltd. SOFT–JECT S6100–CTT 100 ml), then the plunger was inserted. Next 50 ml of a plating solution heated to operating temperature was sucked into the syringe and residual air was carefully ejected. The syringe was maintained at the operating temperature with a water bath. Gas generated during electroless plating pushed up the plunger as illustrated in Fig. 1. The volume of gas generated after plating for 25 min was recorded and the amount of platinum deposited by the increase in weight of the test piece.

2.4. Electrochemical analysis of the films

The electrochemical characteristics of the deposited film were investigated by cyclic voltammetry (CV). Electrochemistry was performed using a three electrode setup with a potentiostat (Ivium Technologies IviumStat) equipped with a platinum wire as the counter electrode, and an Ag/AgCl reference electrode. The working electrode for CV measurement was prepared following the procedures described above. When platinum plated COP sheet was used as the working electrode, it was cut into an appropriate size as to set into the measurement cell (ALS Co., Ltd. Plate Material Evaluating Cell). The thickness of all the deposits was between 0.3 and 0.4 μm. The CV measurements were carried

Table 1
Electroless platinum plating bath compositions and plating conditions.

HYD bath		SBH bath	
$Pt(NH_3)_6Cl_4$ (mmol dm^{-3})	10	$Pt(NH_3)_6Cl_4$ (mmol dm^{-3})	5
NH_3 (28%) aqueous solution (vol%)	6	NaOH (mmol dm^{-3})	250
Hydrazine hydrate (mmol dm^{-3})	62	$NaBH_4$ (mmol dm^{-3})	13
Glycine (mmol dm^{-3})	2.7	Ethylenediamine (mmol dm^{-3})	170
Lead monoxide (μmol dm^{-3})	0.96	Sodium thiosulfate (μmol dm^{-3})	6.2
Bath temperature (°C)	60	Bath temperature (°C)	60
Bath pH	10.0	Bath pH	12.3

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