

# Effect of rare earth (Ce, La) compounds in the electroless bath on the plating rate, bath stability and microstructure of the nickel–phosphorus deposits

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## Abstract

Effects of added rare earth elements (RE) in the acidic hypophosphite plating bath on the plating rate, bath stability and microstructure of the electroless nickel–phosphorus (EN) deposits were studied. The surface appearance and microstructure were examined under a reflection optical microscope and a scanning electron microscope equipped with an in-situ energy dispersive X-ray spectroscopy, which can evaluate the elemental analysis of deposits. It was demonstrated that the rare earth elements can decrease grain size and refine microstructure.

The deposition rate of the Ni–P deposits was estimated by gravimetric, polarization and quartz crystal microbalance (QCM) methods. Results revealed that up to an optimum concentration of rare earth elements, the deposition rate increases. The stability test method was used to determine the stabilization effect of RE on the stability of the bath. It was found that the addition of RE significantly improved the Pd stability of the EN bath.

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## 1. Introduction

Since the discovery of electroless or autocatalytic nickel plating, it has been widely used in electronics machinery, automobile, aerospace and other industries [1,2]. With excellent properties such as non-magnetic, low internal stress and high corrosion resistance, Ni–P alloy coating with high-P content has been an important undercoat for computer hard disks [3].

Rare earth elements have many special properties, such as magnetic, optical, and electric and hydrogen storage properties and have been successfully used in many fields such as metallurgy, electronics and chemical engineering [4,5]. Researchers have found that the rare earth elements can influence on certain parameters like deposition rate and stability of the bath in Cr, Ni and Cu electroplating process, [6–10]. It is also reported that these elements improve mechanical properties of alloys, like tensile strength, toughness and fatigue resistance in alloys such as Al–Li and Al–Si [11].

In the present study, the effects of added rare earth elements (RE) in acidic hypophosphite plating bath on the properties of the resulting electroless Ni–P deposits were studied. The authors found that the addition of rare earth elements can increase the plating rate and bath stability, and improve the film microstructure by refining the grains of deposits.

## 2. Experimental details

### 2.1. Materials and reagents

The gold plated quartz crystals and mild steel coupons were used as the substrates. The chemicals used in the experiments, all purchased from Merck, were of reagent grade and used without any further purification. The used EN solution bath was formulated as Table 1. It was chosen because a glycine–citrate combination produces a complex with nickel and makes the plating solution stable [12]. The initial pH value of the plating bath was adjusted by dilute NaOH solutions to  $4.5 \pm 0.1$ . De-ionized water was used for solutions preparation and rinsing of glassware. Using a digitally controlled thermostat (Memert), the bath temperature was controlled within  $85 \pm 1$  °C under atmospheric environment. The plating was conducted by immersing one piece of the substrate into EN solution (100 ml) in a 150 ml beaker for 1 h.

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Table 1  
Bath composition and deposition conditions

Composition	Condition
NiSO <sub>4</sub> ·6H <sub>2</sub> O	30 g dm <sup>-3</sup> pH 4.5±0.1
NaH <sub>2</sub> PO <sub>4</sub> ·H <sub>2</sub> O	25 g dm <sup>-3</sup> t 85±1 °C
CH <sub>3</sub> COONa	20 g dm <sup>-3</sup>
H <sub>2</sub> NCH <sub>2</sub> COOH	20 g dm <sup>-3</sup>
Ce (IV) Sulfate, La nitrate	0–1 g cm <sup>-3</sup>
Pb (NO <sub>3</sub> ) <sub>2</sub>	2 mg dm <sup>-3</sup>
NaOH	for adjusting pH

## 2.2. Apparatus and experimental procedures

Three methods were used for plating rate measurements. These were gravimetric, polarization and QCM methods.

### 2.2.1. Gravimetric method

In this study, the mild steel coupons (99.47% Fe) were used as the substrates. The steel coupons were polished with the abrasive papers from 400 to 1000 grade, cleaned in concentrated NaOH and activated by acid dip in 30% HCl. The plating rate ( $R$ : mg cm<sup>-2</sup> h<sup>-1</sup>) of the electroless Ni–P alloy was determined by gravimetric method and was expressed in terms of the weight gain during the deposition process. An analytical balance (Unimatic CLX40) with a precision of 0.1 mg was employed to weigh the as-deposited samples. The plating rate was calculated according to the following formula: where  $t$  is the plating duration (min),  $M_t$  (mg) is the mass of the object plated for a length of time,  $M_0$  (mg) is the initial weight of substrate and  $A_s$  is the surface area of specimen (cm<sup>2</sup>) [13].

$$R = \frac{(M_t - M_0) \times 3600}{A_s \times t}$$

### 2.2.2. Polarization measurements

The electrochemical measurements were carried out using an electronic potentiostat (Autolab PG-stat 30). The working electrode was freshly electroless nickel deposited iron plated sized 1 by 1 cm. The auxiliary electrode was a platinum electrode and a saturated calomel electrode (SCE) used as a reference electrode. Linear scanning voltammetry (LSV) was used to plot anodic and cathodic polarization curves. The scan rate was 1 mV/s. According to the steady state equilibrium potential, the rate of reduction (deposition) of metal is equal to the rate of oxidation of reducing agent i.e. [14]:

$$i_{\text{dep}} = i_{\text{m}} = i_{\text{red}}$$

### 2.2.3. QCM method

Quartz crystal microbalance studies were performed using a Maxtec PM-710 plating monitor coupled with a MPS-550 sensor probe, the equipment is calibrated automatically. The Maxtec quartz resonators were made from AT-cut quartz crystals (resonance frequency, 5 MHz having a resolution of the order of 0.5 Hz, which translates to a thickness resolution of 10 ng cm<sup>2</sup>) covered by evaporated gold on both faces (apparent electrode areas, 0.316 cm<sup>2</sup> for the “small” side,

1.37 cm<sup>2</sup> for the “large” side). The quartz crystal was incorporated in a sensor probe made of PTFE.

One O-ring ensures that the liquid comes in contact with one side of crystal only (large side). The oscillator circuit was housed in the probe head. Frequency changes were converted to mass loading using the Sauerbrey formula [15,16].

### 2.2.4. Bath stability test

The Palladium stability test method was used to determine the effect of rare earth elements on the stability of the bath. This test was directed at the lower temperature of 65±1 °C to amplify the difference in stabilities of the plating solutions. When the solution temperature reached to 65±1 °C, 5 ml of 40 mg/l PdCl<sub>2</sub> was added to the solution and the time required for the solution to be decomposed was recorded. The end point or the onset of bath decomposition was defined as the time when the solution became dark green and opaque [17].

### 2.2.5. Surface analysis

The surface morphology of the Ni–P deposits was investigated using optical microscope at low magnitude (×100) in reflected mode and the scanning electron microscopy (LEO 440i). Energy dispersive X-ray spectroscopy (EDAX) with a detection limit of ~0.5 wt.% for most elements was used to analyze the Ni and P content (wt.%) of the Ni–P deposits.

## 3. Results and discussion

### 3.1. The effect of rare earth elements on the plating rate of electroless Ni–P

Table 2 shows the rates of electroless Ni–P deposition obtained from gravimetric and polarization methods in the presence of various concentrations of rare earth compounds. It displays that the additives in the plating bath are able to increase plating rate in a range of optimum concentrations.

Table 2  
Measured parameters for different concentration of cerium and lanthanum

Experimental method	Gravimetric		Polarization		QCM
	T=85 °C		T=85 °C		T=50 °C
Substrate	Rate	$i_{\text{dep}}$	$R_p$	Rate	Rate
	(mg cm <sup>-2</sup> hr <sup>-1</sup> )	(mA cm <sup>-2</sup> )	(ohm)		(mg cm <sup>-2</sup> h <sup>-1</sup> )
Nickel	13.6	1.73	23.47	1.85	0.56
Ce 3 ppm	18.3	2.76	18.50	3.01	0.56
Ce 6 ppm	22.6	2.84	18.79	3.09	0.56
Ce 8 ppm	20.1	2.10	18.85	2.28	0.56
Ce 10 ppm	18.4	2.08	18.70	2.27	0.56
Ce 20 ppm	18.0	1.61	27.03	1.75	0.56
Ce 200 ppm	16.5	–	–	–	0.00
Ce 1000 ppm	7.9	–	–	–	0.00
La 2 ppm	19.4	2.48	18.91	2.70	0.56
La 4 ppm	18.2	2.87	30.23	3.13	0.56
La 5 ppm	19.0	2.43	18.03	2.65	0.56
La 10 ppm	22.4	2.89	17.35	3.15	0.56
La 20 ppm	17.10	–	–	–	0.56

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