Electrochemical investigations on the influence of electrolyte composition of Watts baths with special regard to throwing power

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Abstract

The influence of a variety of substances on technically relevant parameters of a nickel electroplating electrolyte (Watts bath) has been investigated. Special attention has been paid to the throwing power (TP), as well as visual appearance, current efficiency and codeposition of foreign atoms. Systems reported in the literature (e.g., inorganic salts to increase conductivity or complexing agents to increase polarization) were compared with typical reducing agents normally used in electroless Ni deposition. The mechanism of TP improvement in the case of sodium hypophosphite and dimethylamine-borane has been examined with the electrochemical quartz crystal microbalance (EQCM). Using the EQCM it was shown that there is a synergistic effect between the electrochemical and electroless deposition process. In addition, the activation energy of the latter was determined from temperature dependent measurements.

List of symbols

- \(A\) area
- \(C\) proportionality factor in the kinetic equation, describing the temperature dependence of the electroless plating rate
- \(C_{SB}\) Sauerbrey constant
- \(E_A\) activation energy
- \(i\) current density
- \(k\) Wagner parameter
- \(L\) distance ratio in the Haring–Blum cell
- \(m\) mass
- \(M\) mass ratio in the Haring–Blum cell
- \(R\) gas constant
- \(T\) absolute temperature
- \(U\) electric potential
- \(t\) time
- \(\Delta f\) frequency shift
- \(\kappa\) electrolytic conductivity

1. Introduction

Electrochemical nickel plating is a widely used process. Applications comprise functional coatings, for example, for corrosion protection, increase of wear resistance and decorative coatings such as bright Ni mostly in combination with chromium. Many electrolyte formulations are based on the classical composition proposed by Watts, which yields dull Ni deposits. To obtain decorative deposits with a mirror-like surface finish special additive formulations have been developed, which contain organic substances like surfactants, brighteners and levellers. The current efficiency is nearly 100% over a wide range of current densities. However, it is difficult to obtain a uniform deposition thickness distribution on complex shaped substrates, as a consequence of the nonuniform current density distribution. For the majority of applications a uniform thickness distribution on irregularly shaped substrates is desired, which requires an electrolyte with good throwing power (TP).

Empirical investigations have shown that the TP increases with cathodic polarization and with electrolyte conductivity [1]. These two quantities have been summarized in a theoretical treatment by Wagner (Wagner parameter \(k\), Equation 1) [1, 2]:

\[
k = \kappa \left( \frac{dU}{dt} \right)
\]  

The Wagner parameter, \(k\), which should be proportional to the TP, increases with increasing electrolyte conductivity \(\kappa\) and the slope of the polarization curve \((dU/di)\) under steady conditions.

In the electroplating industry an assessment of the TP is done by determining the thickness of the plating on a cathode, or several electrically connected cathodes, as a function of the distance from the anode. The
Haring–Blum cell or the Hull cell are widely used experimental set-ups. The percentage TP can be calculated with the relation given by Field (Equation 2):

\[
TP = \frac{L - M}{L + M - 2} \times 100
\]

where \( L \) is the ratio of the distances of the cathodes from the anode, and \( M \) is the ratio of the deposited masses. Usually a distance ratio of 5:1 for the cathodes is used. The determination of TP is described in [3, 4].

Recently, it has been found that the TP of a Watts electrolyte is increased by adding sodium hypophosphite [5]. Hypophosphite is used in electroless Ni deposition, because it acts as a reducing agent for Ni ions. Therefore, an investigation was carried out to examine the relation between an increase in TP and the reducing properties and to analyse the individual contributions of the electrochemical and the electroless deposition processes. The electrochemical quartz crystal microbalance (EQCM) proved to be a valuable tool for these investigations. Frequency shifts of a quartz crystal are related to changes in the areal mass density at its surface by the Sauerbrey relation (Equation 3) [6]:

\[
\Delta f = -C_{SB} \left( \frac{m}{A} \right)
\]

where \( \Delta f \) is the shift of the resonance frequency of the quartz crystal, \( m/A \) the areal mass density, and \( C_{SB} \) the Sauerbrey constant (226.014 Hz cm\(^2\) l g\(^{-1}\) for a 10 MHz quartz, see Section 2).

Besides the effect of hypophosphite, the influence of sulphur-, boron- and phosphorous-containing reducing agents and some organic substances was studied, some of which have been proposed as possible candidates to improve the TP. Another aim of the work was to investigate how these substances influence the visual appearance of the deposits, the codeposition of foreign atoms and the current efficiency.

### 2. Experimental details

The electrolytes examined were based on a typical Watts bath, containing 0.17 M NiSO\(_4\)·6H\(_2\)O, 0.77 M NiCl\(_2\)·6H\(_2\)O (both purity 98%, Grüssing GmbH, Germany), 0.65 M H\(_2\)BO\(_3\) (99.5%, Riedel de Haen). The pH value was adjusted to 4.2 ± 0.2 with 1 M NaHCO\(_3\) or 2 M H\(_2\)SO\(_4\). An electrolyte for bright Ni deposition was obtained by adding a commercial additive formulation (Duplalux G, wetting agent Ni 719 and a ‘brightness correction solution Ni’, Atotech, Berlin, Germany) to this electrolyte. Table 1 lists the investigated substances together with their concentration ranges in the electrolytes (Watts or bright Ni electrolyte). Highly purified water was used for the preparation of all solutions.

Polarization curves for the determination of the Wagner parameter (Equation 1) were measured using an EG&G 263A potentiostat (PAR, Oak Ridge, USA) in a thermostated glass cell (55 ± 1 °C). The working electrode was a rotating (500 rpm) Ni disc of 0.28 cm\(^2\) surface area. A saturated calomel electrode (SCE) was used as reference electrode and a Ni sheet as counter electrode. All potentials are quoted with reference to the SCE. The electrolytes were purged with nitrogen at least 10 min prior to the experiment. The conductivity of the electrolytes was measured at room temperature with a conductivity meter.

The substrates for the galvanostatic depositions were degreased with CH\(_2\)Cl\(_2\), activated in 1M HCl + 2 M H\(_2\)SO\(_4\), rinsed with deionized water, immersed in 2 M H\(_2\)SO\(_4\), and thoroughly rinsed again. The determination of the TP followed the procedure by Haring and Blum [7] in a double jacketed cell (made in-house, poly(eth-

### Table 1. Investigated substances, concentration range and their effect on the Wagner parameter and the TP

<table>
<thead>
<tr>
<th>Substance</th>
<th>(c) /mol l(^{-1})</th>
<th>Wagner parameter*</th>
<th>TP*</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid (C(_3)H(_4)(OH)(COOH)(_3))</td>
<td>0.100–0.800</td>
<td>++</td>
<td>++</td>
<td>h.c.d.: white blooming</td>
</tr>
<tr>
<td>Tartaric acid (C(_4)H(_2)(OH)(_4)O(_2))</td>
<td>0.029–0.095</td>
<td>--</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Mannite (C(_6)H(_8)(OH)(_6))</td>
<td>0.082–0.330</td>
<td>--</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Sodium dithionite (Na(_2)S(_2)O(_4))</td>
<td>decomposition in the electrolyte during the deposition fine-grained black precipitation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium disulfite (K(_2)S(_2)O(_5))</td>
<td>0.002–0.045</td>
<td>--</td>
<td>--</td>
<td>h.c.d.: black loose deposits</td>
</tr>
<tr>
<td>alone or with 0.040 M MgSO(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watts electrolyte, Bright Ni electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hypophosphite (Na(_3)H(_2)PO(_2))</td>
<td>0.047–0.189</td>
<td>0</td>
<td>++</td>
<td>l.c.d.: black bloomy coating</td>
</tr>
<tr>
<td>Watts electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium phosphite (Na(_2)HPO(_3))</td>
<td>0.005–0.100</td>
<td>not detd.</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Bright Ni electrolyte, Watts electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethylamine-borane (DMAB) (CH(_3))(_2)NHBH(_3)</td>
<td>0.017–0.160</td>
<td>not detd.</td>
<td>++</td>
<td>non-uniform visual appearance</td>
</tr>
<tr>
<td>Bright Ni electrolyte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Code: (++) increase, (+) slight increase, (0) no effect, (−) slight decrease, and (−−) decrease with increasing concentration of the corresponding substance.