FACTORS AFFECTING THE ELECTROLESS DEPOSITION OF Ni-Cu-P COATINGS
J. Georgieva, S. Armyanov,
Institute of Physical Chemistry,
Bulgarian Academy of Sciences,
Sofia 1113, Bulgaria

Independently on the way of their preparation, the addition of copper affects the non-magnetic stability of amorphous Ni-Cu-P alloys in two ways (1, 2). First, Cu content up to 5 w/o is increasing the crystallization temperature. Second, the magnetic phase precipitated during devitrification is enriched in copper, which reduces its magnetic moment, as well as the total alloy magnetization. Among the numerous usual and new applications of the electroless Ni-Cu-P alloys, aiming an improvement of Ni-P properties, it is worth mentioning the investigation of Ni-Cu-P utilization as underbump metal for the flip-chip solder bump structure (3).

These reasons justify the interest in electroless plating of Ni-Cu-P, which is being conducted since 1972. Recently a simple model describing the codeposition of copper during electroless plating of this ternary alloy has been proposed (4). Until now the influence of the traditional complexing agents, pH and bath temperature on the alloy composition and plating rate has been examined in a classical way, without considering in details the possible interactions between these (variable) factors.

The aim of this investigation is to achieve empirical modeling of the electroless Ni-Cu-P deposition process. Similar approach has been applied to electroless Co-P (5). In our study a full factorial design (FFD) at two levels of the process variables is selected. Our objective is by applying the above statistical techniques to the electroless deposition of Ni-Cu-P, to detect the interactions between variables, to build a model of the plating process and to construct the response surfaces.

Electroless deposition of Ni-Cu-P was carried out from a solution enabling the introduction of copper without reducing the content of phosphorus, which is very important for the thermal stability. The applied bath is shown in Table 1 and it is based on our previous investigations (4, 6). The deposition temperature was 88ºC and pH 4.7.

<table>
<thead>
<tr>
<th>Components</th>
<th>mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄ · 6H₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>NaH₂PO₂ · H₂O</td>
<td>0.36</td>
</tr>
<tr>
<td>CH₃COONa · 3H₂O</td>
<td>0.20</td>
</tr>
<tr>
<td>C₆H₅Na₃O₇ · 2H₂O</td>
<td>0.15</td>
</tr>
<tr>
<td>C₂H₄NO₂</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu (II) in the solution, ppm</td>
<td>15</td>
</tr>
</tbody>
</table>

Three independent variables were chosen: solution acidity pH, citrate and glycine concentration. Controlled parameters of the process were the deposition rate and the alloy composition presented by Cu and P content in w/o.

The obtained Ni-Cu-P coatings were smooth and bright. They were amorphous and with good adhesion to the substrate. The elemental composition of the plated alloys was determined using energy dispersive spectroscopy (EDS). In addition, copper content was determined by atomic absorption spectroscopy (AAS). One of the obtained response surfaces is shown in Fig. 1.

Fig. 1. Response surface for the copper content 2.5 w/o (by AAS) as a function of citrate and glycine concentrations and pH.

CONCLUSIONS
1. Adequate models have been obtained enabling the estimation of the effect of pH and complexing agents (citrate and glycine) concentration on the deposition rate and Ni-Cu-P alloy composition. Interactions between all pairs of variables have been found.
2. The deposition rate and the copper concentration in the alloy are affected the most powerfully by pH and citrate concentration. Phosphorus content depends mainly on the citrate concentration in the bath. Within the range of factors variation in the current FFD experiment pH does not affect strongly P content in the alloy.
3. It may be concluded from the obtained models that all three controlled parameters (deposition rate, Cu and P content in the alloy) have been affected by both citrate and glycine concentration, though the effect of glycine is weaker.

REFERENCES