Preparation and Electric Resistance Evaluation of Electroless NiReP Alloy Films as a Thin Film Resistor

Tetsuya OSAKA*, Takayuki HOMMA, Makoto FUKAWA, Hiroshi IWAMOTO and Jun KAWAGUCHI†

Received April 2, 1991 ; Accepted May 17, 1991

1. INTRODUCTION

Recently, electroless plated thin films have been applied to thin film resistors1–2). Amorphous electroless NiP alloy films have been usually used as a thin film resistor featuring its high specific resistance, low TCR (temperature coefficient of resistance) and excellent corrosion resistivity. When these films are applied to a thin film resistor for severer atmosphere such as annealing during production processes, it is necessary for them to have the sufficient thermal stability. We reported that the codeposition of refractory metals such as tungsten or molybdenum into electroless NiP alloy film is effective for improving its thermal stability3–5). This paper takes into account that rhenium is also refractory metal, and describes the effect of its codeposition into electroless NiP alloy film on its thermal stability focusing upon its electric resistance properties.

Table 1 Bath composition and operating conditions of electroless NiReP alloy films.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration / mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂HPO₄·H₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>C₆H₄OH(COONa)₂·2H₂O</td>
<td>0.40</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.075</td>
</tr>
<tr>
<td>NH₄ReO₄</td>
<td>0·030</td>
</tr>
</tbody>
</table>

pH 9.0 (adjusted with NaOH and H₂SO₄)
Bath temperature 80°C

2. EXPERIMENTAL

Electroless NiReP alloy films were plated from a bath with the composition listed in Table 1. The film thickness was adjusted to 1.5 μm by controlling deposition time. The contents of rhenium and phosphorus were determined by an inductively coupled argon plasma emission spectrophotometer (ICP). The values of TCR were calculated from the temperature-resistance diagrams in the range of -60°C to 70°C. Surface morphology of the film was observed with a scanning electron microscope (SEM). The structure of the film was examined by an X-ray diffractometer (XRD). The other detailed procedures have been described elsewhere4–5).

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of NH₄ReO₄ concentration on specific resistance and the contents of rhenium and phosphorus. With an increase in the NH₄ReO₄ concentration, the specific resistance value of the electroless NiReP alloy films increased up to 3,600 μΩ cm, which is about twenty-five times as large as that of electroless NiP films. The SEM observa-
tion indicated that such a high specific resistance value was not due to surface cracks caused by inner stress of the film. It was also confirmed in Fig. 1 that a large amount of rhenium can codeposit into electroless NiP alloy film plated from the bath listed in Table 1. In particular the film plated from the bath containing 0.030 mol dm\(^{-3}\) of NH\(_4\)ReO\(_4\) shows such a high specific resistance value. Therefore we focus upon the film properties in detail.

In order to study thermal stability of the alloy film, heat change behavior of resistance property was investigated. Figure 2 shows the effect of heat-treatment temperature on specific resistance and TCR values of the film. The specific resistance value at as-plated conditions is as high as 3,600 \(\mu\)cm, however, it decreases steeply down to 330 \(\mu\)cm after heat-treatment at 200°C. This result suggests that thermodynamical properties of the film at as-plated conditions are very unstable. The TCR value of the samples heat-treated even at 500°C, however shows an excellent property as 18 ppm K\(^{-1}\).

In order to study the correlation between resistivity and structure after heat-treatment, the films were examined with XRD. The XRD results clarified that the film has an amorphous or microcrystalline structure at as-plated conditions. The micro-crystalline structure was also maintained after heat-treatment at 500°C, and the peaks due to crystallization appeared after heat-treatment at 600°C.

In general application for resistors, electroless Ni alloy films are usually pre-annealed to improve their thermal stability\(^2\). Considering the results described above, therefore, the heat-treatment at 500°C is adequate for thermal stabilization of the electroless NiReP alloy film. Figure 3 shows the change in resistance of the film annealed at 500°C. For comparison, the thermal stability of the resistance of electroless NiWP\(^4\) and NiMoP\(^5\) is also shown. As is clearly seen in Fig. 3, the NiReP film demonstrates the most excellent thermal stability among the three Ni alloy films.

In summary, codeposition of rhenium is effective for improving thermal stability of pre-annealed electroless Ni alloy films although electroless NiReP alloy film at as-plated conditions is unstable against heat-treatment.

Fig. 3 Change in resistance of electroless Ni\(_{51}\)Re\(_{44}\)P\(_{5}\) (at\%) alloy film (annealed at 500°C for 1h), electroless Ni\(_{49}\)W\(_{20}\)P\(_{6}\) (at\%) alloy film (annealed at 400°C for 1h) and electroless Ni\(_{54}\)Mo\(_{46}\)P\(_{6}\) (at\%) alloy film (annealed at 500°C for 1h) during heating at a rate of 10°C min\(^{-1}\).

REFERENCES