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Electroless Nickel Plating onto Minute Patterns of Copper Using Ti(III)/Ti(IV) Redox Pair

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Reducing agent employed for Ni electroless plating includes phosphinic acid, sodium borohydride, and hydrazine. When phosphinic acid and sodium borohydride are used, P and B are codeposited with Ni film, respectively, while the use of hydrazine results in the inclusion of nitrogen as an impurity. Such nonmetallic components in Ni film are often detrimental for the use of magnetic materials. In the field of semiconductor devices, the use of Ni containing P and B is sometimes avoided since they act as dopants for silicon semiconductor, resulting in a lowering of the reliability of the device. Against such a background, a novel electroless plating using Ti(III)/Ti(IV) redox pair was investigated,[1] where Ti(III) ions act as reducing agent. A pure Ni film can be obtained with the use of the reducing agent Ti(III), since oxidation of the agent does not accompany the irriversible decomposition of Ti(III) ions but the change in oxidation number of Ti(III) ion only changes from +III to +IV. In addition, Ti(III) ions can be regenerated by the reduction of Ti(IV) ions.[2] In the present work, selectivity of electroless Ni plating onto a minute area was examined using Ti(III) ions and the reactions were discussed thermodynamically.

A bath (0.04 M $NiSO_4$, 0.08 M $TiCl_3$, 0.24 M citric acid, and 0.04 M nitrilotriacetic acid, 50 ˚C) with stabilizer and accelerator was employed for the plating. pH of the bath was adjusted with 25% aqueous ammonia. In addition to Cu plates, TEG (test element group) substrates with Cu and SiO_2 patterns were used to examine the selectivity of the plating. The resulting deposits were analyzed with SEM (scanning electron microscope, XRF (X-ray fluorescence analyzer), and EPMA (electron probe micro analyzer). Mass of the deposits was measured in-situ with electrochemical QCM (quartz crystal microbalance) with sputtered Au electrodes.

Bright Ni films were obtained on a Cu plate using the bath with a pH of 7.5-9. Plating reaction did not proceed under pH 7.5, and the plating bath was decomposed over pH 9. In the pH range 7.5-9, the deposition rate of Ni increased with increasing pH of the bath. The most effective and stable condition was pH 8.4. Ni was not deposited on SiO_2 but on a minute Cu square area of 5 µm on a side by dipping TEG substrate into the bath with a pH of 8.4 (Fig. 1). Ni plating onto a minute Cu interconnection area on TEG with 160 nm in width was also performed successfully (Fig. 2). These indicated that the Ni plating bath can be used for a selective plating to a submicron-sized minute area. The deposition rate and the concomitant change of immersion potential were examined by the use of QCM substrate (Fig. 3,4). The initial deposition rate of Ni was found to be about 3 nm min^{-1} and the plating rate was suppressed with the passage of plating time. Thickness of Ni film was controllable by plating time from several 10 nm to over 100 nm. The immersion potential continued to increase with the passage of plating time from about –0.75 V vs. SHE even after the suppression of the plating, suggesting that some electrochemical reactions other than the actual plating reaction concurrently took place. pH of the plating bath decreased with time, because of the reductive decomposition of H_2O with the oxidization of Ti(III) ions into TiO^{2+} ions.

1. S. Inazawa *et al*., *Hyomen Gijutsu*, **53**, 694 (2002).
2. S. Inazawa *et al*., *Hyomen Gijutsu*, **54**, 488 (2003).

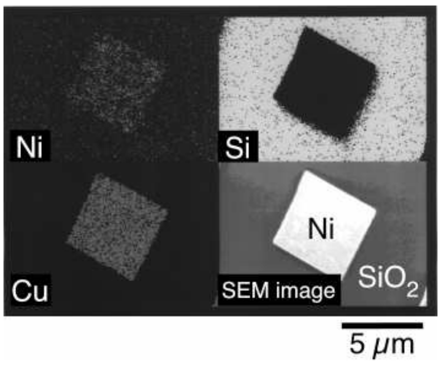

Figure 1. Analysis of a minute Cu square area of 5 µm on a side on TEG substrate by EPMA after Ni electroless plating.

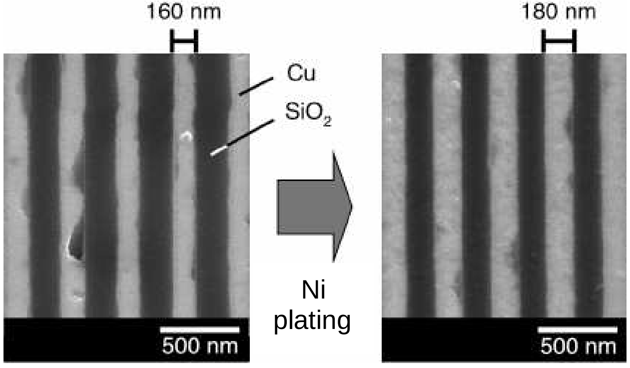

Figure 2. SEM images of Cu interconnections of 160 nm in width on TEG substrate before and after Ni electroless plating.

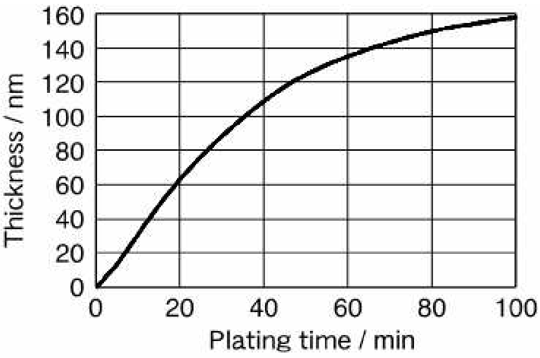

Figure 3. Change in thickness of Ni film deposited on the QCM substrate with the passage of plating time.

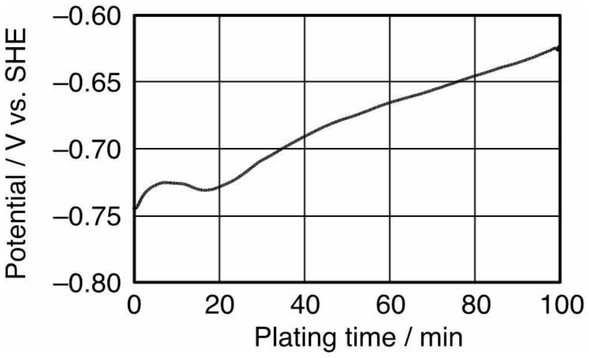

Figure 4. Change in immersion potential of QCM substrate with the passage of plating time.