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Partial nickel plating using organic gel electrolyte

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Abstract

A partial nickel plating method was developed by using the organic gel electrolyte. The gel electrolyte was made from polyvinylchloride as a gelling agent and tetrahydrofuran as an organic solvent. The suitable conditions for nickel plating were investigated by the measurements of polarization curve and electrochemical impedance. The pattern electroplating using thin layer of gel electrolyte was carried out on the copper substrate. The substrate surface could be plated by nickel with high uniformity and sharp edge line. The present method will be widely used for the surface patterning without masking.

Keywords: Organic solvent; Gel electrolyte; Nickel plating; Partial plating; Electrochemical impedance

1. Introduction

Partial plating is a technique for coating only in the specific part on a substrate. Partial plating has been used for the repairing damaged part of the film and available for the surface patterning. Brush plating is one of the useful and portable methods of the partial plating without masking [1–4]. A brush attached to anode is dipped in a plating solution and then contacted on the specific part of a cathode substrate. It is difficult for this method to control the surface area precisely with good reproducibility. Besides, laser plating has been examined for partial plating [5], but it requires laser equipment, which is generally large and expensive.

There are some reports regarding the research for the partial plating with the aqueous gel electrolyte as follows: (a) plating used agar as gelling agent to manufacture probe pin [6] and (b) copper plating from copper sulfate solution gelated by gelatin [7]. The authors [7] reported various electrochemical measurements for copper plating with gel electrolyte, and clarified the reaction mechanisms and the roles of additives. In this method, the pattern plating can be carried out with the use of a small amount of the electrolyte by thinning its thickness and the pattern can be drawn with the gel easily and precisely without masking.

In the present study, we developed a new partial nickel plating method by using the organic gel electrolyte. Nickel electroplating has been widely used for the industrial products because of their excellent corrosion resistance, hardness, and beautiful externals with silver-white color. However, nickel electroplating from an aqueous electrolyte solution, like Watt solution [8], is usually accompanied by hydrogen generation. The cathode current efficiency of some aqueous nickel electroplating solutions may vary from 90% to 97% [8]. If an aqueous electrolyte solution was used in the partial plating using the gel electrolyte, the electrodeposition of nickel was inhibited by absorption of the hydrogen on the substrate. Therefore, we use the organic solvent for the electroplating solution because of the wide potential window.

An aim of this research is development of the nickel partial plating with organic gel electrolyte and analysis of the nickel electrodeposition in the gel electrolyte by using the electrochemical impedance spectroscopy (EIS).

2. Experimental method

2.1. Gel electrolyte

$Ni(ClO_4)_2 \cdot 6H_2O$, LiCl and $LiClO_4$ were used for the electrolytes. LiCl and $LiClO_4$ act as the complexing agent and supporting electrolyte, respectively. Tetrahydrofuran (THF,

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Wako Chemical) was used for an organic solvent. Polyvinylchloride (PVC, degree of polymerization: 1100, Wako Chemical) was used for a gelling agent. Gel electrolyte was prepared by adding PVC in the THF electrolyte. All chemicals used in the present paper were the analytical grade. Molecular sieve was used for the purification of THF electrolyte. All experiments were carried out under a dry argon atmosphere in a glove box.

2.2. *Measurement of cathodic polarization curve and electrochemical impedance*

Cathodic polarization curve and electrochemical impedance were measured for the analysis of the nickel electrodeposition in the gel electrolyte. These measurements were performed using the three electrodes method. Pure copper rod (Nilaco, grade: 99.5%) was used for working electrode whose diameter was 5.0 mm. Nickel plate was used for the counter electrode. The reference electrode was Ni wire. In the present paper, the potential is represented relative to the Ni reference electrode. Before the measurement, the surface of the working electrode was polished with emery papers down to grid size #2000. After polishing, the working electrode was cleaned in methanol and distilled water successively.

The *i*–*E* curve was measured by using the potentiostat (Hokuto, HG-501G) connected with the potential sweeper (Hokuto, HB-111). The potential was scanned at 0.1 V/min, and the response current was recorded by the personal computer.

The electrochemical impedance was measured by using the high response potentiostat (Hokuto, HG-501G) and the frequency response analyzer (FRA, NF circuit block 5020) controlled by a personal computer through GP-IB interface. The impedance measurement was carried out in a frequency range from 10 mHz to 10 kHz. The amplitude of the potential modulation of the working electrode was 10 mV. The measurement of electrochemical impedance was started at 30 min after polarization at an arbitrary potential to obtain the steady state.

The surface of the electroplated film was observed by using the scanning laser microscope (Keyence, VK-8500) and analyzed by GD-OES (Horiba, JY-5000RF).

2.3. *Partial plating of nickel on the copper surface*

Partial plating was performed on a copper plate in galvanostatic electrolysis using the two electrodes method. A copper plate (Nilaco, grade: 99.9%) was used for cathode. A nickel plate was used for the anode. To mold the thin film of gel electrolyte, the electrolyte was injected into the various size of the template. Then, the gel layer thickness was equal to the template thickness. The anode was put on the gel electrolyte. The current density was set at $-1\ \mathrm{mA/cm^2}$. The electrode surface after plating was photographed with a digital camera. Before the measurement, the surfaces of the cathode and anode were soaked for 5 min by the degreasing agent (Okuno Seiyaku, Ace Clean) followed by polishing with alumina powder (diameters: 0.05 μm). After polishing, the electrode was cleaned in methanol and distilled water successively.

Table 1
Viscosity of the THF solution containing various concentration of PVC

	Viscosity (Pa s)
THF (PVC 0 wt%)	5.9×10^{-4}
PVC 5 wt%	1.3×10^{-2}
PVC 10 wt%	8.2×10^{-2}

3. Results and discussion

3.1. *The preparation of gel electrolyte*

We chose THF as the solvent because the THF dissolved many kinds of electrolytes. THF has been applied for electroplating with organic solvent, especially the electrodeposition of alminum with high throwing power [9–11]. The PVC was chosen as a gelling agent. PVC has been used as the gelling agent in a wide variety of fields. PVC is quite stable in THF. In addition, PVC is employed as a brightener in THF electroplating bath [11].

Table 1 shows the viscosity of THF electrolyte containing various concentrations of PVC. The viscosity of the solution increased with the increase of PVC concentration. The THF electrolyte containing 0–10 wt% PVC behaved as the Newton fluid. On the other hand, the electrolyte containing 15–20 wt% PVC was the non-Newton fluid and behaved as a gel. The viscosity cannot be measured more than 20 wt% PVC, since 10^5 Pa s is upper limit of the present measurement. In these results, we have decided that THF electrolyte containing 20 wt% PVC was used for the gel electrolyte.

3.2. *Measurement of cathodic polarization curve*

The cathodic polarization curves of copper electrode in a gel electrolyte containing various concentration of $Ni(ClO_4)_2\cdot6H_2O$ and LiCl were shown in Fig. 1. The gel electrolyte contained equimolar amounts of $Ni(ClO_4)_2\cdot6H_2O$ and LiCl because LiCl was used as the complexing agent for nickelous ion. The cathodic

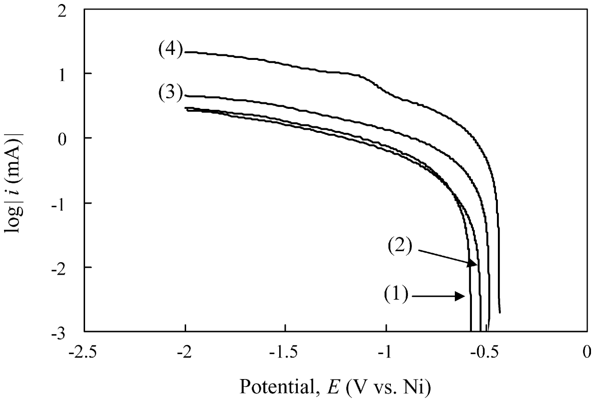

Fig. 1. The cathodic polarization curves of copper in the gel electrolyte (20 wt% PVC) containing $NiClO_4\cdot6H_2O$ and LiCl: (1) 0 mol/dm^3, (2) 0.05 mol/dm^3, (3) 0.1 mol/dm^3, and (4) 0.5 mol/dm^3. All the gel electrolytes contained 0.1 mol/dm^3 $LiClO_4$ as a supporting electrolyte. The concentration of polyvinylchloride (PVC) was 20 wt%. The potential sweep rate was 0.1 V/min.

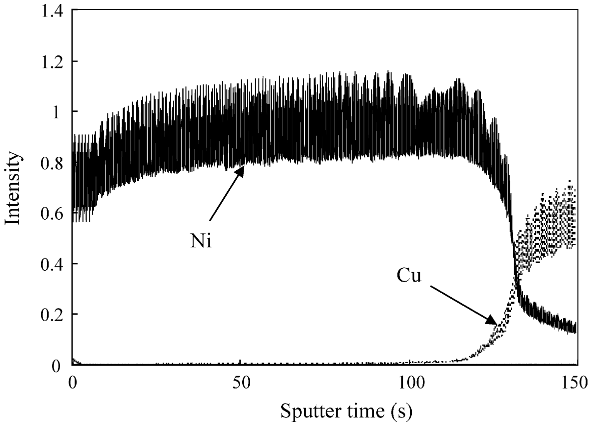

Fig. 2. The depth profile of the electroplated film performed on a copper sheet in the electrolyte containing 0.5 mol/dm^3 $NiClO_4 \cdot 6H_2O$ and 0.5 mol/dm^3 LiCl. The film was electroplated by the potentiostatic electrolysis at −1.0 V vs. Ni, 50 °C, and analyzed by GD-OES measurement.

currents were observed at the potential region between −0.5 and −2 V. The blank current ((1) in Fig. 1) would be caused by a non-Faraday process. The cathodic current increased with the increase of the concentrations of $Ni(ClO_4)_2 \cdot 6H_2O$ and LiCl. After the measurement, it was observed that the electrode surface was coated with the silver-white film.

The GD-OES measurement was carried out to obtain the depth profile of the silver-white film (Fig. 2). It was found that the film contained only Ni. The impurities such as other metals are not detected. In addition, the current efficiency of the electroplating evaluated from the mass change between before and after the measurement was approximately 99%. The hydrogen gas generation was not observed in the potential area between 0 and −2.5 V. These results indicate that the nickel plating from the organic gel electrolyte can be performed with high purify and high current efficiency.

3.3. Measurement of the electrochemical impedance in the gel electrolyte

Fig. 3 shows the Nyquist plots of electrochemical impedance measured at various potentials (−0.4, −0.6, −0.8, −1.0 V) in the gel electrolyte containing 0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, and 0.5 mol/dm^3 LiCl. A small inductive loop was observed in Fig. 3(1) and (2) The inductive loop observed at the low frequency range was found to be the Faradaic impedance due to the adsorbed intermediate [12,13]. The reaction mechanism of the nickel electrodeposition was proposed as the two-step reaction ($Ni(II) \rightarrow Ni(I)_{ad} \rightarrow Ni$) [14], and the adsorbed intermediate would be $Ni(I)_{ad}$. Therefore, the nickel would deposit at the two-step reaction in the organic gel electrolyte. The values of solution resistance (R_{sol}) evaluated from the intersection of real axis at high frequency side were about 50 Ω cm^2 in Fig. 3.

In Fig. 3(3) and (4), Warburg impedance was observed in low frequency range. From the results of Fig. 3(3) and (4), it was found that the contribution of diffusion to the electrodeposition mechanism was small since the Warburg impedance was observed at only narrow potential range.

3.4. Influence of the gel electrolyte thickness for the electrodeposition of nickel

It is important for high quality plating to keep the nickel concentration in the gel electrolyte. The surface concentration of nickelous ion is concerned with the mass transfer of the nickelous ion from the anode to the cathode. However, the diffusion rate of the nickel ion might be smaller than that in aqueous solution. Therefore, it is necessary to investigate whether the gel electrolyte thickness influences on the cathodic reaction or not.

The influence of the gel electrolyte thickness was investigated by using two electrodes method. The electroplating was

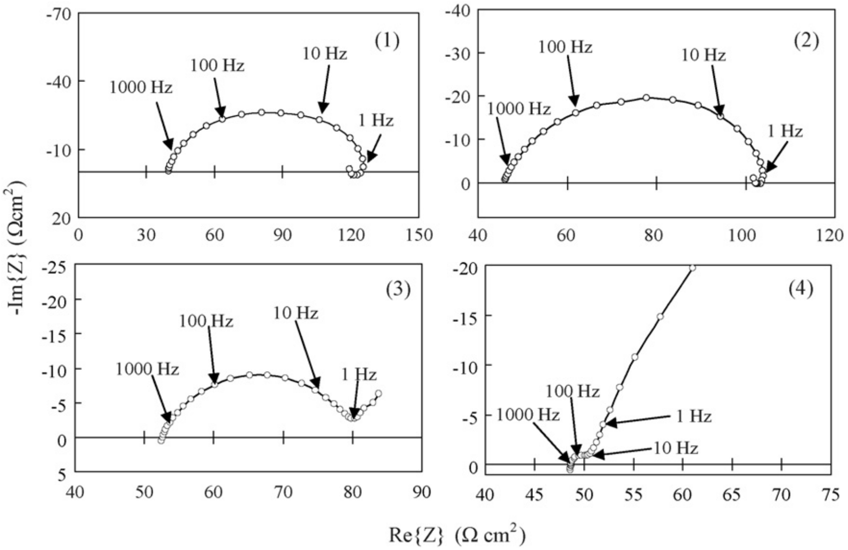

Fig. 3. Experimental results of the electrochemical impedance of copper in the gel electrolyte containing 0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, 0.5 mol/dm^3 LiCl. The potentials were (1) −0.4 V, (2) −0.6 V, (3) −0.8 V, and (4) −1.0 V.

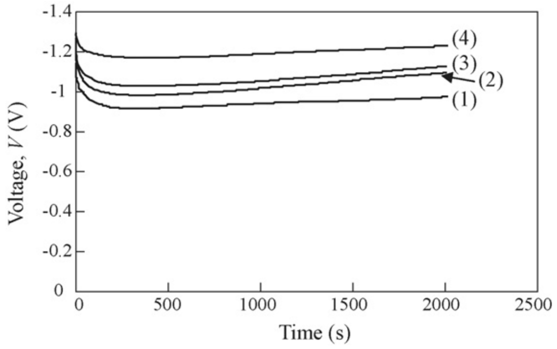

Fig. 4. The cell voltage and time curves during nickel electrodeposition at various thicknesses of gel electrolyte (0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, 0.5 mol/dm^3 LiCl). The thicknesses of gel electrolyte were (1) 3 mm, (2) 5 mm, (3) 7 mm, and (4) 12 mm. The current density was -1 mA/cm^2.

performed at -1 mA/cm^2. The gel electrolyte thickness was varied between 3 and 12 mm. The V–t curves were shown in Fig. 4. The plating time was set at 2000 s. The voltage arises in the early stage, and became constant after 500 s. The rapid increase of voltage which caused degradation of electrolyte was not observed at any sample. The voltage between two electrodes aroused as the gel layer thickness increased. Fig. 5 shows the photographs of electrode surface observed by confocal laser scanning microscope after nickel deposition at various thicknesses of gel electrolyte. The smooth surface with luster was observed regardless of the gel layer thickness. From the results above-mentioned, it was found that the gel layer thickness between 3 and 12 mm had no effect for the cathodic electrodeposition and the anodic dissolution. Therefore, it makes possible to plate with a small volume of the gel electrolyte.

3.5. Measurement of the electrochemical impedance using the two electrode method

From the results of the V–t curve in the Section 3.4, it was found that the voltage between two electrodes increased with the increase of gel layer thickness. The voltage (V) is expressed by

$$V = V' + iR_{\mathrm{sol}} \tag{1}$$

where V', i and R_{sol} were voltage induced by the concentration polarization between two electrodes, imposed current and solution resistance, respectively. According to Eq. (1), the R_{sol} increase with the increase of V. Consequently, the values of R_{sol} and other reaction parameter at the various thickness of the gel electrolyte were estimated by the electrochemical impedance method.

Fig. 6 shows the Nyquist plots of electrochemical impedance measured at various thickness of the gel electrolyte. A capacitive loop was observed in the fourth quadrant and a part of an inductivity loop was observed in the first quadrant in Fig. 6. The equivalent circuit for an electrode/solution interfaces at two electrodes cell is shown in Fig. 7. In Fig. 7, R_{ct1} and R_{ct2} represent the charge transfer resistance. C_1 and C_2 are the capacitance of the electric double layer at two electrodes. R_{L} and L represent the resistance and inductance, respectively to represent the inductive loop. The electrochemical parameters evaluated by the curve-fitting were shown in Table 2. The R_{sol} value rises with the increase of the gel layer thickness linearly. On the other hand, the values of R_{ct} were constant without depending on a gel layer thickness. From these results, it was confirmed that the voltage (in Fig. 4) increased with the increase of the R_{sol} value depending on the gel layer thickness. Therefore, it was found that the dissolution/electrodeposition reactions were not influenced by a

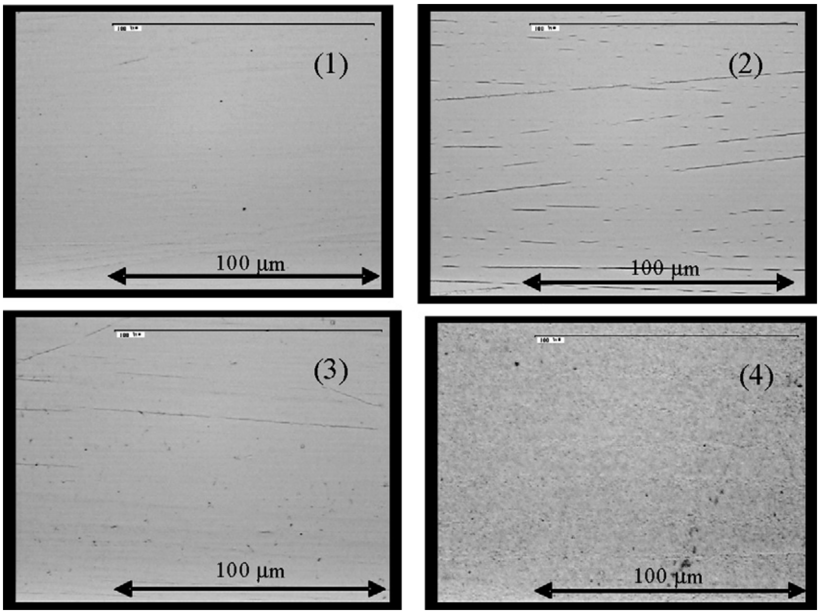

Fig. 5. Photographs of electrode surface after nickel deposition at various thicknesses of gel electrolyte (0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, 0.5 mol/dm^3 LiCl) by confocal laser scanning microscope. The thicknesses of gel electrolyte were (1) 3 mm, (2) 5 mm, (3) 7 mm, and (4) 12 mm. The applied current density was -1 mA/cm^2. The plating time was set at 2000 s.

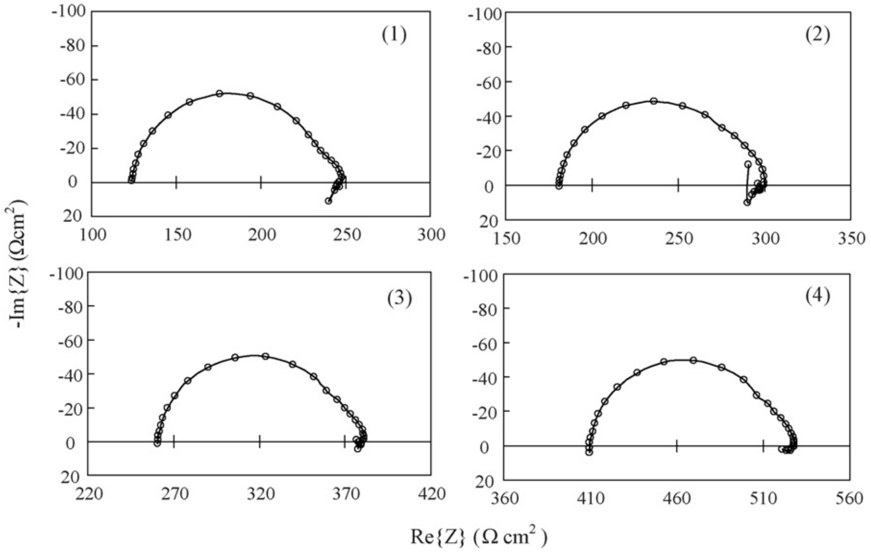

Fig. 6. Experimental results of the electrochemical impedance of copper in the gel electrolyte containing 0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, 0.5 mol/dm^3 LiCl at various thicknesses of gel electrolyte. The thicknesses of gel electrolyte were (1) 3 mm, (2) 5 mm, (3) 7 mm, and (4) 12 mm.

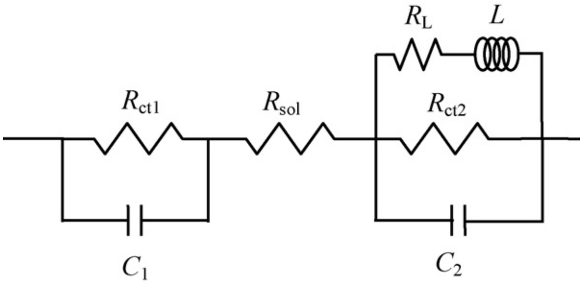

Fig. 7. Equivalent circuit for an electrode/solution interface at two electrode cell.

gel layer thickness. From these results, it makes possible to plate with high current efficiency by thinning down the gel electrolyte thickness.

3.6. Pattern plating of nickel

The pattern plating of nickel was performed on a copper substrate by the galvanostatic electrolysis in a gel electrolyte. The current density was −1 mA/cm^2. The plating time was set at 2000 s. The average thickness of the gel electrolyte was about 0.55 mm. Fig. 8 shows photographs of the substrate and the counter electrode surface after plating observed by using the digital camera. The substrate surface plated had high uniformity and sharp edge line. In addition, the counter electrode was dissolved stably. It makes possible to perform the gel pattern plating of nickel using organic solvent.

Table 2
Electrochemical parameter derived by curve fittings

	Membrane thickness			
	3 mm	5 mm	7 mm	12 mm
R_{ct1} (Ω cm^2)	19.3	24.1	21.4	19.0
C_1 (×10^{-4} F)	4.51	1.93	3.03	4.02
R_{sol} (Ω cm^2)	125	185	262	411
R_{ct2} (Ω cm^2)	103	93.78	97.1	97.6
C_2 (×10^{-6} F)	7.16	8.19	8.29	8.82

Fig. 8. The photographs of (a) cathode and (b) anode after the pattern electroplating using gel electrolyte. The gel electrolyte contained 0.5 mol/dm^3 $Ni(ClO_4)_2 \cdot 6H_2O$, 0.5 mol/dm^3 LiCl. The cathode substrate was copper. The current density was −1 mA/cm^2. The average thickness of gel electrolyte was about 0.55 mm. The plating time was set at 2000 s.

4. Conclusion

The electroplating of nickel with the organic gel electrolyte has been studied. THF and PVC were chosen as the organic solvent and the gelling agent, respectively.

The influences of the nickelous ion concentration on the reaction mechanisms of nickel electroplating were investigated by electrochemical impedance spectroscopy. A small inductive loop was observed at high and low frequency ranges. The reaction mechanism of the nickel electrodeposition was proposed as the two-step reaction (Ni(II) → $\mathrm{Ni(I)_{ad}}$ → Ni).

The electroplating in the gel electrolyte was performed by using two electrodes method. By means of the adjustment of the gel electrolyte thickness, the pattern plating of nickel can be performed to a copper substrate by the galvanostatic electrolysis in a gel electrolyte. The nickel can be plated on the copper substrate surface with high uniformity and sharp edge line.

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