Electroless and Electrolytic Plating of Ni, Cu, and $Co_xFe_{2-x}O_4$ for the Application of Three-Dimensional Micro-Molding

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We investigated the combination of electroless and electrolytic plating of nickel, copper, and ferrite onto photopolymerized resin for use in the molding of three-dimensional micro-structures. The micro-molding process consists of four steps: fabrication of the resinous mold via two-photon micro-polymerization, plating of the mold, electrolytic grinding to open the interior structure, and extraction. A non-conductive epoxy resin was plated with nickel, copper, or ferrite through the electroless process, and then, the second layer composed of the other material was grown by the electroless or electrolytic plating. We found that the every combination of the three materials is available. The electrolytic plating was useful for applying a thick film with high purity.
Keywords: electroless plating, electrolytic plating, microstructure, molding, photopolymerization

1. Introduction

Micro electro mechanical systems (MEMS) are now widely used in our society. However, they are made from semiconductors, and metal is not used in the body due to its difficulty in micro-processing. If mechanical characteristics and special properties of metal, such as magnetism, high conductivity, and shape memory effect, are available, the application field of MEMS will be widely expanded. Micro-fabrication with photopolymerized resin is regarded as one of the alternative micro-part production technologies because of its suppleness, easiness, and quickness [1 - 3]. However, due to the weakness of the resin against environmental factors (e.g., high temperature, acidity and alkalinity), there are some limits to its practical use.

We have proposed a novel micro-molding method for the fabrication of metal and metal-compound microstructures [4, 5]. Our micro-molding process consists of four major steps. First, raw resin is polymerized by scanning with a focused laser beam to form the mold of microstructure. The resolution of the polymerization is now as low as 30 nm when using the two-photon absorption method [6]. Next, the non-conductive polymer mold is coated through electroless plating. In this step, the inner space of the negative shape is filled by the metal or metal compound. Then, the obstructive is removed by electrolytic grinding, and the opening of the mold is exposed. It should be noted that the electrolytic grinding stops by itself when the inner metal and outer coating are electrically isolated [7]. Thus, a precise cut is attained at the opening of the mold. Finally, the microstructure is extracted by removing the resin. In our previous work, the electroless plating conditions for nickel, copper, and ferrite were found on the epoxy resin subjected to two-photon polymerization, and the extraction of the nickel and copper microstructure from the resinous mold was

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achieved [5, 8]. The electrolytic plating was also investigated after the electroless plating on the resinous mold to make the plated body sufficiently thick with short process time and good crystal quality [9].

In this paper, we investigated the combination of electroless and electrolytic plating of nickel, copper, and ferrite on the photopolymerized resin for use in the molding of three-dimensional micro-structures. After the non-conductive epoxy resin was plated with nickel, copper or ferrite through the electroless process, the other material was attached on the first film by the electroless and electrolytic plating. High-resolution optical microscope was used to observe the interface of the double-layered films. X-ray fluorescence measurements were used to evaluate the purity of the layers.

2. Multiplication of electroless plating with different materials

We examined the creation of a double-layered film on a photo-polymerized resin by means of a hybrid process of nickel, copper, or ferrite electroless plating. An epoxy resin suitable for the two-photon polymerization was used for the experiments. A circular cup made of silicone was prepared, and the pellet-shaped resin was polymerized in the cup. An ultraviolet (UV) lamp was used for the polymerization for the convenience of sample preparation. The diameter of the sample was 5 mm, and the thickness was 3 mm. Before the electroless plating, the surface of the resin was rinsed out with pure water and acetone under ultrasonic waves.

For the nickel electroless plating [5], the sample was immersed in the catalytic solution composed of 0.2 g/L $PdCl_2$ + 3.0 g/L $SnCl_2$ + 150 mL/L HCl at 30°C for 5 minutes. Subsequently, the sample was immersed in the plating solution, composed of 21 g/L $NiSO_4$ + 22 g/L $C_2H_5O_2N$ + 4.0 mg/L PbO and 20 g/L NaH_2PO_2. The plating solution was continuously stirred during plating. The temperature was 45°C, and the pH was maintained at 8.1 - 8.4 using NaOH.

For the electroless plating of copper on the photopolymer surface, the plating procedure is almost the same as that for the nickel electroless plating. After washing and catalysis, the sample was immersed in the plating solution. The composition of the plating solution was 15 g/L $CuSO_4{\cdot}5H_2O$ + 53 g/L CH_2O + 40 g/L $C_4H_4KNaO_6{\cdot}4H_2O$ (Rochelle salt) + 25 g/L H_2NCH_2COOH. The plating temperatures was 25°C, and the pH was controlled at 12.5 - 13 using NaOH.

For the electroless plating of ferrite onto photopolymerized resin, we also cleaned the samples in water and acetone using ultrasonic waves. Without catalysis, the samples were immersed in a bath, where the 12 g/L $FeCl_2{\cdot}4H_2O$ + 9.5 g/L $CoCl_2{\cdot}6H_2O$ plating solution and the 7.0 g/L $NaNO_2$ + 15 g/L CH_3COONH_4 oxidizing solution were injected [9]. The injection rate was 5 cm^3/min for both solutions. The mixed solution was homogenized using a temperature-controlled hot plate stirrer. The reaction temperatures was 80°C, while the pH of the oxidizing solution was controlled at 7 - 8 using NH_3.

We investigated the combination of nickel and copper electroless plating. Without any surface treatment, with only water washing, both the plating of copper on the nickel film and that of nickel on the copper film were succeeded. Fig. 1 shows high-resolution optical microscope images of the cross-section of a double-layered plated film. Fig. 1(a) shows the nickel film on the copper film on the resin, and Fig. 1(b) shows the copper film on the nickel film on the resin. The total thickness of both film is about 20 μm. The border between the two layers is approximately in the middle of the film. However, the border is not distinguishable by the optical microscope observation. There was no void or crack between the layers. We saw that the coherency between the films was very good.

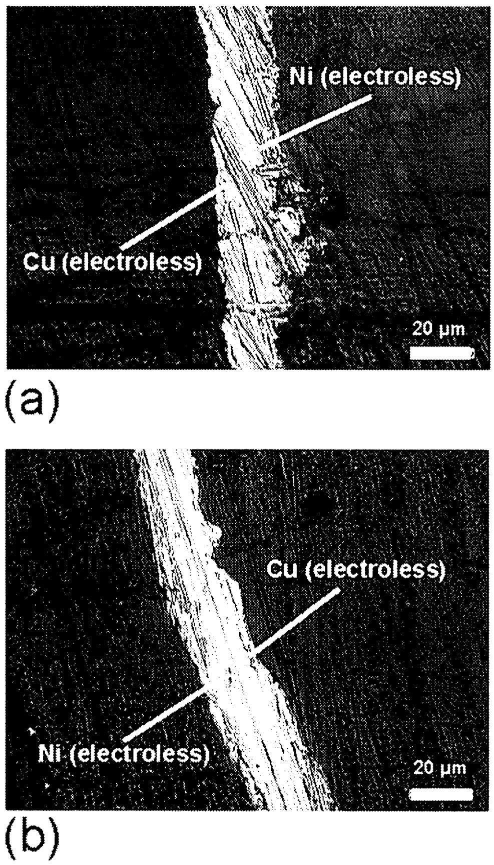

Fig. 1 High-resolution optical microscope images of the cross-section of a double-layered film formed by the electroless plating: (a) the nickel film on the copper film, and (b) the copper film on the nickel film. The left-hand side is epoxy resin. For observation purposes, the film surface was supported by another plastic.

We next investigated the formation of the nickel or copper layer on the ferrite layer on the resin. The metal layer was not formed on the ferrite without any surface modification. We found that the catalytic process after the ferrite formation was effective to grow metal layers. Fig. 2 shows high-resolution optical microscope images of the cross-section of a double-layered plated film. In the figure, the left-hand side is epoxy resin again. Figure 2(a) shows the copper film on the ferrite film on the resin, and Figure 2(b) shows the nickel film on the ferrite film on the resin. In both figures, the interface of the layers is clearly seen owing to the high contrast of the layers. The interface is very rough in the order of microns. We can see that the rough interface was completely

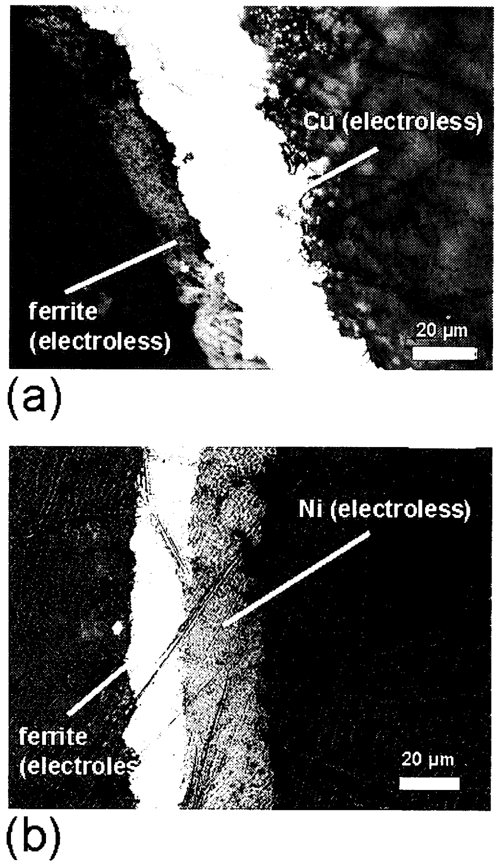

Fig. 2 High-resolution optical microscope images of the cross-section of a film formed by the electroless plating: (a) the copper film on the ferrite film, and (b) the nickel film on the nickel film.

buried by the metals.

We also investigated the ferrite electroless plating on the nickel or copper layer. The ferrite layer was difficult to grow on the metal layers. The catalysis was not effective to the ferrite electroless plating. Because the ferrite electroless plating requires OH-basis on the surface, we oxidized the metal surface in electric furnace. At the thermal oxidation, the copper film was processed at 150°C for three hours, and the nickel film was processed at 360°C for three hours. After the platings, we observed high-resolution optical microscope images of the cross-section of a double-layered film. Fig. 3(a) shows the ferrite film on the nickel film on the resin, and Figure 3(b) shows the ferrite film on the copper film on the resin. We saw again that the highly-contrasted

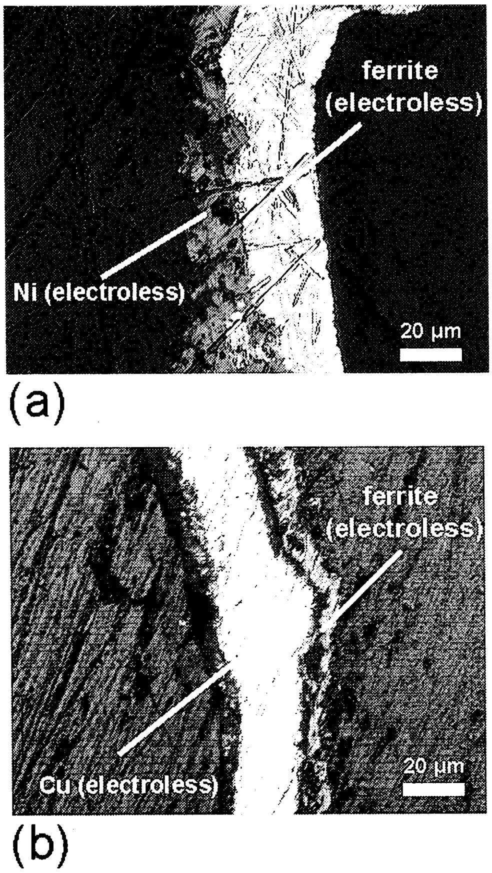

Fig. 3 High-resolution optical microscope image of the cross-section of a film formed by the electroless plating: (a) the ferrite film on the nickel film, and (b) the ferrite film on the copper film:

interface was very rough and completely buried by the ferrite without void or clacks

The results presented in this section clearly suggest that the formation of the multiple layers of nickel, copper, and ferrite is available by the electroless plating with close adhesion.

3. Combination of electroless plating and electrolytic plating

We investigated the combination of electroless plating and electrolytic plating for the multiplication of layers with different materials. Because the resinous mold is non-conductive, the first layer must be formed by the electroless plating. However, once the conductive layer is formed on the surface, the additional layers can be formed by the electrolytic plating, which is advantageous to get the film with high purity and low crystal distortion [8]. We tried to form the nickel and copper film with the electrolytic plating on the metal-coated surface. The electrolytic plating of ferrite has not yet been succeeded, to our knowledge, even on the metal plate.

For the electrolytic nickel plating, we used a Watt's bath solution (195 g/L $NiSO_4 \cdot 7H_2O$ + 174 g/L $NiCl_2 \cdot 6H_2O$ + 40 g/L H_3BO_3). The temperature of the Watt's bath was 45°C. The sample was connected at a cathode, and the nickel metal plate was used as an anode. The current density was about 0.1 - 1.0 mA/mm^2. The growth rate of the plated film was 60 μm/h, which is equivalent to 24 times that in electroless plating.

For the electrolytic copper plating, the plating solution of 50 g/L $CuSO_4 \cdot 5H_2O$ + 8 g/L H_2SO_4 was used. The temperature of the plating solution was 25°C. The sample was connected at a cathode, and the copper metal plate was used as an anode. The current density was about 0.1 - 1.0 mA/mm^2. The growth rate of the plated film was 76 μm/h.

The electrolytic plating was performed with only water washing after the formation of first film with the electroless plating. We observed high-resolution optical microscope images of the cross-section of the plated film. Fig. 4(a) shows the copper film formed by the electrolytic plating on the copper film formed by the electroless plating. Fig. 4(b) shows the nickel film formed by the electrolytic plating on the copper film formed by the electroless plating. The border between the electrolytic plating and electroless plating is approximately in the middle of the film, but the border is not distinguishable in both optical microscope observation. We found that the coherency between the films was very good.

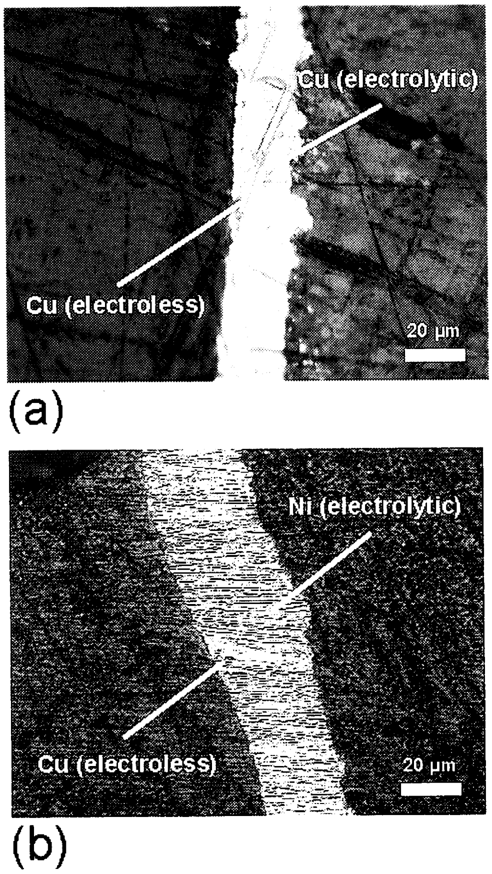

Fig. 4 High-resolution optical microscope images of the cross-section of a plated film: (a) the copper film formed by the electrolytic plating on the copper film, and (b) the nickel film formed by the electrolytic plating on the copper film.

Table I Components of the first layer and the second layers plated with electroless and electrolytic process. "UDL" means "under the detection limit".

	1st (electroless) Cu (mass%)	2nd (electrolytic) Cu (mass%)	Ni (mass%)
Ni	UDL	UDL	94.8
Cu	58.4	99.2	UDL
O	21.2	UDL	UDL
Na	12.8	UDL	UDL
Cl	3.9	UDL	2.0
S	UDL	0.8	1.4

X-ray fluorescence was measured to evaluate the components of the plated film. As seen in Table I, the purity of copper is quite better (more than 99 %) in the second layer than in the first layer. In the first copper layer, chlorine is expected to be originated from the catalytic solution, and sodium is from the plating solution. In the second nickel layer, we did not detect the signal that suggests the composite of copper from the first layer.

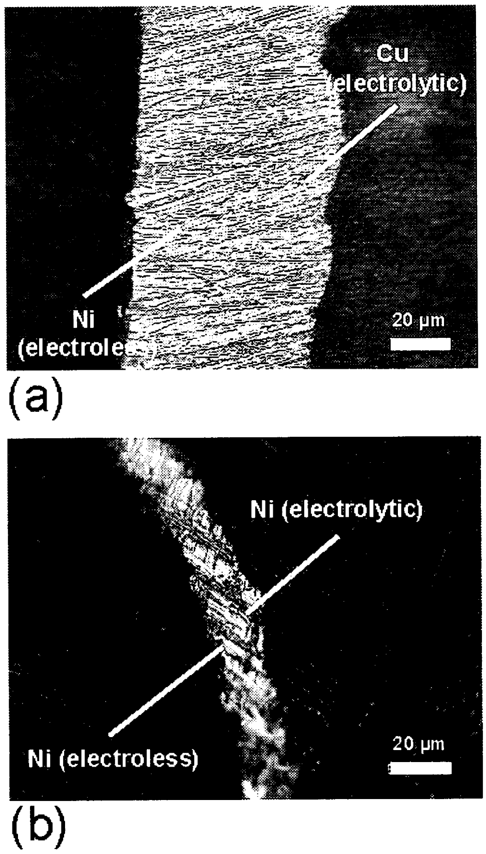

Fig. 5 High-resolution optical microscope images of the cross-section of a plated film: (a) the copper film formed by the electrolytic plating on the nickel film, and (b) the nickel film formed by the electrolytic plating on the nickel film.

The samples with the nickel first layer was observed by the high-resolution optical microscope. Fig. 5(a) shows the copper film formed by the electrolytic plating on the nickel film, and Fig. 5(b) shows the nickel film formed by the electrolytic plating on the nickel film. The border between the electrolytic plating and the electroless plating is not distinguishable again in both microscope observations. We can see that the coherency between the films was very good like the sample with the copper first layer.

X-ray fluorescence was measured to evaluate the components of the plated film using the nickel first layer (Table II). We can see that the purity of nickel is better in the second layer than in the first layer. In the first nickel layer, chlorine is expected to be originated from the catalytic solution. Phosphorus and sodium are expected to be originated from the plating solution. In the second copper layer, we did not detect the mixture of nickel from the first layer.

Table II Components of the first layer and the second layers plated with electroless and electrolytic process. "UDL" means "under the detection limit".

	1st (electroless)	2nd (electrolytic)	
	Ni (mass%)	Ni (mass%)	Cu (mass%)
Ni	92.8	95.9	UDL
Cu	UDL	UDL	89.2
Cl	0.3	1.7	UDL
P	4.3	UDL	UDL
Na	2.0	UDL	UDL
S	UDL	0.9	1.9

We have investigated the combination of the first ferrite layer and the second nickel or copper layer using electrolytic plating process. Although the metal grew partially occasionally, it did not usually grow on the ferrite at all due to the high electric resistance. However, it should be noted that we can grow both copper and nickel film on the ferrite film with electroless plating. Once the metal coats the whole ferrite surface, the electrolytic plating will be available to create the metal second layer with high purity on the ferrite film.

4. Conclusion

We investigated the combination of electroless and electrolytic plating of nickel, copper, and ferrite on the photopolymerized resin for use in the molding of three-dimensional micro-structures. A non-conductive epoxy resin was plated with nickel, copper, or ferrite through the electroless process, and then the second film composed of the other materials was formed on the first film by the electroless and electrolytic plating. In some cases, catalysis process or thermal oxidation is required, but every combination of these three materials was available. X-ray fluorescence measurements revealed that the second metal layer grown by the electrolytic plating had high purity and did not contain the first layer's metal as a contamination. Metal coating on the ferrite film with the electrolytic plating was difficult, but once the metal coats the whole ferrite surface with the electroless plating, the electrolytic plating will be available to create the thick metal layer. Our results will aid in the fabrication of micro electro mechanical system made of multi-layered metal and metal-compound materials.

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