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Ferrite and copper electroless plating to photopolymerized resin for micro molding of three-dimensional structures

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1. Introduction

The three-dimensional microstructure made of metal or metal compound will open up various application fields, owing to their special properties such as mechanical strength, shape-memory effect, magnetism, high conductivity, surface plasmon, etc.. Metal-coated photopolymer microstructure has been developed utilizing stereo lithography of photopolymerized resin and electroless plating on it [1, 2]. The resolution of resin structure can be 100 nm using the two-photon polymerization technique [3]. We have proposed a new fabrication method of microstructures made of metal to the inside [4]. The fabrication process is divided into four main steps (Fig. 1). First, the resin is polymerized to form a mold. Next, electroless plating is applied to the non-conductive resin mold. Then, the obstructive metal plated at the opening of the mold is removed by electrolytic grinding, that stops by itself when the non-conductive resin is exposed. Finally, the microstructure is extracted. We have succeeded in nickel electroless plating to the epoxy resin suitable for two-photon polymerization, and replicated rice grain with nickel in demonstration of the micro molding process. In this study, we apply this method to ferrite and copper and fabricate the small screw.

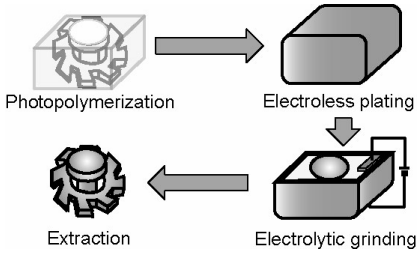

Figure 1 Micro molding process.

2. Ferrite electroless plating

We succeeded in ferrite electroless plating to the photopolymer surface with the equipment shown in Figure 2. After the adequate washing, the sample was set in the bath where $FeCl_2 \cdot 4H_2O$ + $CoCl_2 \cdot 6H_2O$ plating solution and $NaNO_2$ + CH_3COONH_4 oxidizing solution were injected as shown in the figure. Temperature of the bath was controlled and the mixed solution was homogenized on a hot plate stirrer. Ferrite was plated at the temperature of 25, 50, and 80 ˚C and the pH of oxidizing solution was controlled between 6.5 and 10 using NH_3. High resolution optical microscope image of cross section indicated that the small pits of 2 – 5 μm in depth were completely filled by the plated material at the sample surface.

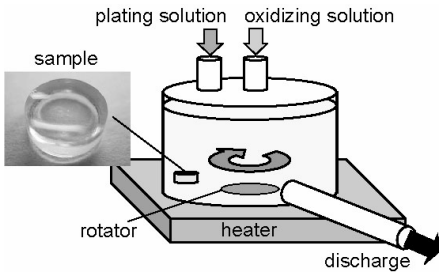

Figure 2 Schematic of experimental equipment for electroless plating of ferrite.

We evaluated the plated film by x-ray diffraction (XRD) measurements. Figure 3 shows the XRD curve. The diffraction peaks were assigned as indexed in the figure, suggesting that the ferrite was successfully plated. X-ray fluorescence measurement revealed the component elements of the plated film and supported the XRD evaluation.

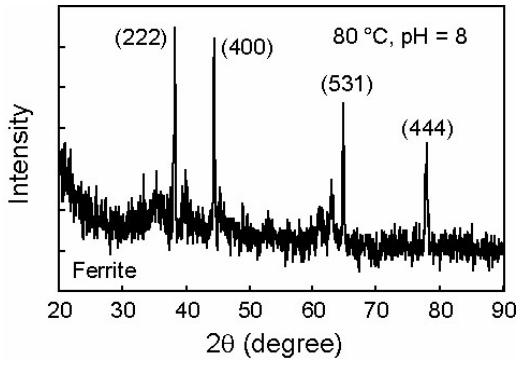

Figure 3 XRD curve of ferrite plated at 80°C with pH = 8 of oxidizing solution.

The full width at half maximum (FWHM) of the diffraction peak is a good index of the residual stress in polycrystal. Figure 4 indicates that pH of oxidizing solution does not affect the residual stress. On the other hand, growth rate of plated film was found to be dependent on pH. It is different in the case of electroless plating of nickel that there is no obvious correlation between growth rate and FWHM of XRD peak.

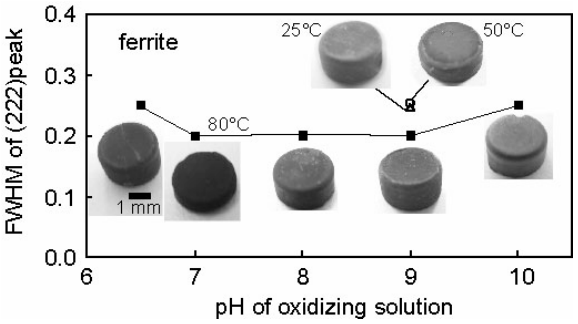

Figure 4 FWHM of a ferrite (222) peak as a function of pH of oxidizing solution. Insets are appearances of samples.

3. Copper electroless plating

We also succeeded in copper electroless plating to the photopolymer surface. The procedure of copper plating is almost the same as nickel's [4]. Sample was immersed in the plating solution composed of $CuSO_4 \cdot 5H_2O$, CH_2O, $C_4H_4KNaO_6 \cdot 4H_2O$, and H_2NCH_2COOH after the catalytic process. Temperature was 15, 25, and 40°C. pH was controlled using NaOH. High resolution optical microscope image indicated that the surface small pits were completely filled by the plated material.

We evaluated the lattice distortion of the plated copper by XRD measurements. Figure 5 indicates the FWHM of Cu(111) XRD peak, that increased as pH of plating solution was raised. The growth rate of plated film doubles as pH is raised in this range. We think that crystal stress due to impurities and dislocations were introduced more with the increase of pH. Metal gloss at the surface changed drastically as shown in the figure. X-ray fluorescence measurement revealed that the purity of the plated film is related to the surface gloss.

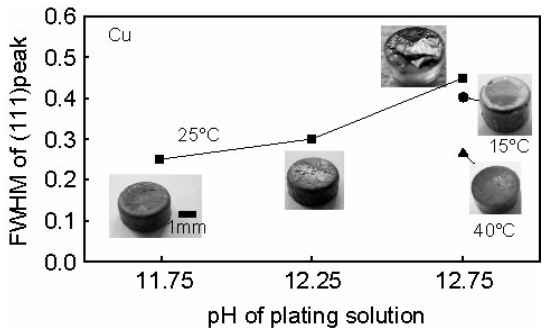

Figure 5 FWHM of Cu(111) peak as a function of pH of plating solution. Insets are appearances of samples.

4. Fabrication with resin mold

We fabricated the shape of screw made of copper using the resin mold. Figure 6 represents the mold and the fabricated structure. The mold was formed by replicating a small screw made of stainless steel. Crack and deformation were generated in the mold at the extraction of the original screw, and therefore, replicated copper structure has the warped shape. The fabricated copper screw has the glossy surface.

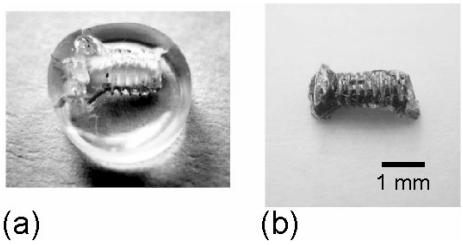

Figure 6 (a) Resin mold of screw shape, and (b) screw made of copper fabricated via the molding process.

Figure 7 shows high resolution optical microscope images at the thread of the screw. The thickness of the original thread was about 40 μm, and that of the copper replica was the same or slightly larger at some places. We suppose that the small size discrepancy owes to the initial deformation of the resin mold.

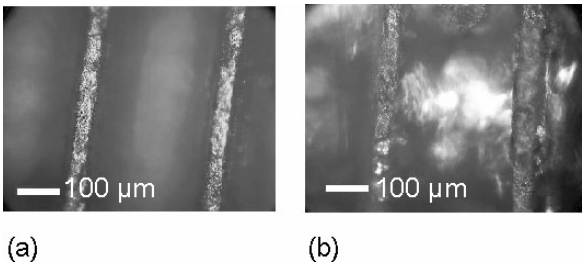

Figure 7 High resolution optical microscope images at the thread of the screw : (a) original and (b) copper replica.

5. Conclusions

The microfabrication process using photopolymerized resin mold was applied to the ferrite and copper. Electroless plating of these materials to the mold succeeded by investigating temperature and pH condition of solution. High resolution optical microscope observation indicated that the several-μm-deep pits at the surface were fully plated by the materials. We fabricated the shape of screw made of copper using the resin mold and found that the structure was formed to a thread of thickness 40 μm precisely.

References

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