Preparation of metal nano particles using electrochemical deposition†

— Pt nano patterned electrodes —

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1. Introduction

Metal nano-particles have been known to possess various properties which cannot be obtained in the bulk phase and are expected to be applied to various fields such as electronics and biotechnology, etc [1-4]. The nano particles are prepared through physical or chemical approaches. The chemical method has advantages for fabricating the nano particles with precisely controlled nano structure. Among the chemical methods, an electrochemical process is utilized in which the nano particles are prepared by reduction at a cathode substrate [5]. In this case, the metal occasionally forms dendritic like growth, which results in non-uniformity of the particles. In order to solve this problem, in this study, we attempt to optimize the surface nanostructure of the cathode. In order to prevent coagulation of the metal particles and achieve numerous nucleation, we applied the nano-dot-patterning to the electrode surface using Pt electrodeposition and UV-NIL processes[6]. Furthermore, we investigated the Pt deposition conditions, mainly focusing upon the effect of additive such as polyethylene glycol(PEG) in order to obtain high surface activity.

2. Experimental

A Ni and a Ti seed layers were deposited onto Si(111) wafer using sputtering. The thickness of the Ni and the Ti layers were 100 nm and 10 nm, respectively. The substrates with the seed layers were cleaned with 14 wt% HCl aqueous solution for 20 s followed by rinsing with ultra pure water, then in order to generate uniform nucleation the specimens were immersed into a 0.2 mM Pd aqueous solution for 300 s followed by rinsing with ultra pure water. After these pretreatments, the Pt was electrodeposited using the bath shown in **Table 1**. The surface morphology was observed using scanning electron microscopy with field emission source (FE-SEM, S-4800, Hitachi) and atomic force microscopy (AFM, Dimension 3100, Veeco Instruments). The composition was analyzed using a glow discharge optical emission spectrometer (GDOES, JY-5000RF, HORIBA).

Table 1 Bath composition for Pt electrodeposition.

Chemicals	Concentration
$H_2(PtCl_6) \cdot 6H_2O$	10 g dm^{-3}
PEG (M. W. 200-20000)	0-100 mM

Figure 1 shows the UV-NIL process for the nano-patterning of the cathode surface patterns. First, UV resin is spin-coated on a Si substrate with a seed layer (1). A stamper with nano patterns is pressed to the substrate and UV light is irradiated from above (2, 3, 4). Then, the stamper is removed from the sample (5). Subsequently, the residual films at the hole are removed using O_2 RIE (6). This substrate with a nano-patterned surface is used as a cathode electrode(7). **Figure 2** shows the schematic illustration of the Pt electrodeposition. A Pt film is deposited on the Si substrate with nano patterns using a rotating disk electrode system. The 100 nm thick Pt films were deposited using HZ-5000 rotating electrode system (HOKUTO DENKO) with a SCE as reference electrode.

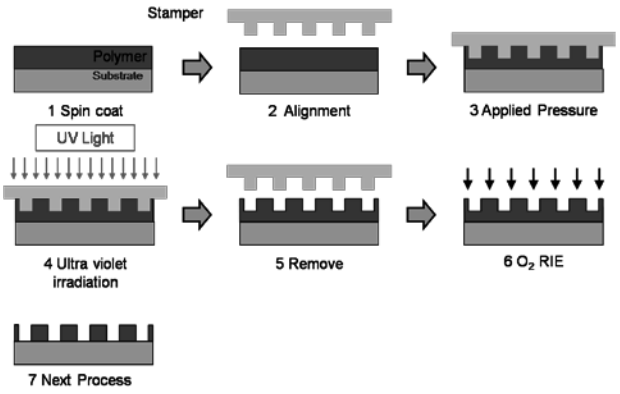

Fig. 1 UV-NIL process.

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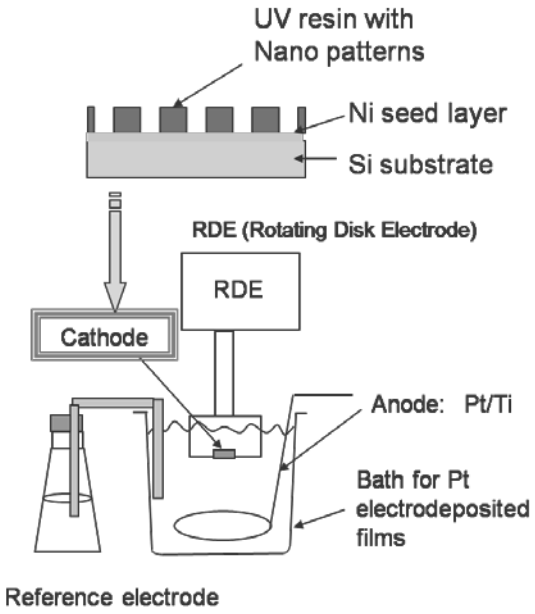


Fig. 2 Schematic illustration of the electrodeposition.

3. Results and Discussion

Figure 3 shows the cathodic polarization curves of the bath for the Pt electrodeposition. The results for the bath with and without additives are shown. As is seen in the figure, the cathodic current was suppressed by adding PEG to the bath. It was confirmed that the PEG acts as inhibitor. Also, the cathodic current decreases with an increase in the molecular weight (M. W.) of the PEG. These results for the behavior of PEG showed the same trends to those observed for Cu electrodeposition for via-filling [7].

Figure 4 shows representative AFM images of the electrodeposited Pt films. As a reference, the image for sputtered Pt film is also shown. From the results, it is confirmed that the electrodeposited Pt films have rougher surface than that of the sputtered film. Moreover, the roughness became larger by the addition of PEG to the bath. On the other hand, as is seen in Fig. 4, when the PEG with larger M. W. such as 20000, is applied, the surface becomes smoother.

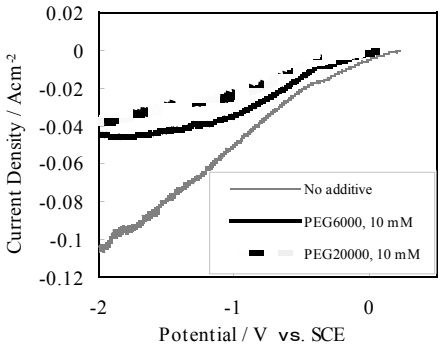


Fig. 3 Cathodic polarization measurement of the bath for the Pt electrodeposition.

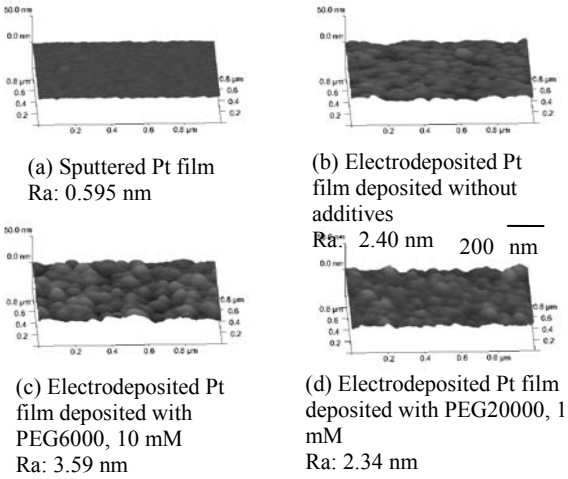


Fig. 4 AFM images of Pt films.

Figure 5 shows the representative results in 0.5 M aqueous sulfuric acid solution. The observed current density of the electrodeposited Pt film was larger than that of the sputtered film. The film deposited from the bath containing PEG exhibited the highest current density among the examined films. These results correspond to those related to the surface morphology described above. Namely, it was suggested that the Pt films with larger surface area or

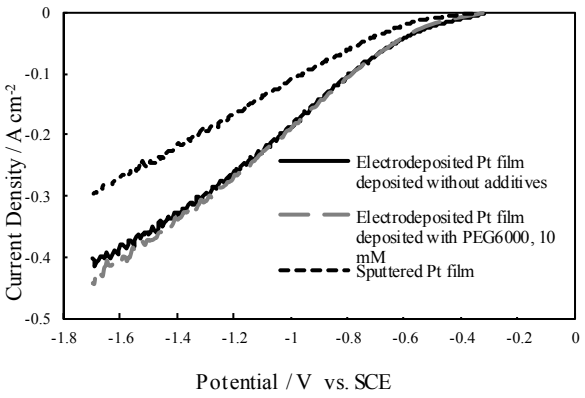
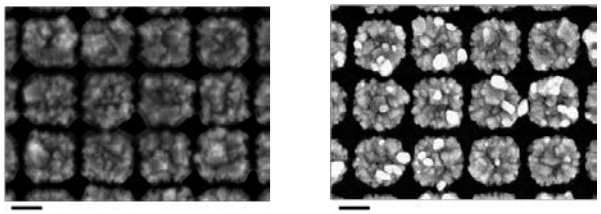


Fig. 5 Cathodic polarization measurement of the Pt films in 0.5 M aqueous sulfuric acid.



(a) Pt nano patterned (b) Cu nano-particles formed on the Pt nano patterned

Fig. 6 SEM images for electrodeposited Pt nano patterned electrode using UV-NIL(a) and Cu nano-particles formed on the Pt nano patterned(b).

larger surface roughness possess larger cathode current flow.

In order to confirm the effectiveness of the Pt nano-patterned electrodes, Cu nano particles were performed with the electrolyte containing Cu-Acetate using the Pt nano-patterned electrodes. **Figure 6** shows representative SEM images of the surface of nano patterned Pt electrode with 400 nm pith periodic structure and Cu nano particles formed on the Pt nano electrode [8]. It was confirmed that the Pt nano-patterned electrodes revealed the ability for preparing Cu nano particles.

4. Conclusions

Electrodeposited Pt nano-patterned electrodes for the formation of nano particles were investigated. In order to achieve higher activity, the deposition conditions of Pt were optimized using additives such as PEG. The surface activity of the Pt films was affected by the size of molecular weight of PEG. It was considered that the Pt films, which have large surface area, exhibited high surface activity among the examined samples. The Pt films, which exhibited the highest current density, were adapted to fabricate nano-patterned electrode with 400 nm pith periodic structure using UV-NIL. It was revealed that Cu nano particles were prepared using Pt nano-dot-patterned electrode.

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