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The effects of pulse-current electrodeposition of nickel on a surface roughness and current efficiency

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Abstract

This paper aims to improve a surface roughness and current efficiency of nickel electrodeposition by a pulse current technique. At nanoscale, the surface roughness of the deposited structure by a pulse current technique was smaller and its current efficiency was improved when comparing with a direct current technique. However, among the pulse current technique within the examined frequency range, i.e. 10-500 Hz, at 50% duty cycle, only small difference could be obtained.

Keywords: Pulse electrodeposition, Surface roughness, Current efficiency, Nickel

1. Introduction

Low cost and an ability to fabricate a high aspect-ratio structure is important in a micro- and nano-scale system industries. One of the key fabrication techniques is a LIGA process that consists of a lithography patterning of a mold and an electrodeposition of targeted metal. Between them, the electrodeposition is significantly important since it directly affects the quality, such as surface roughness, and the operating cost, such as current efficiency, for a fabrication. In general, there are two methods to improve the surface properties and current efficiency. The first method is to add additive to an electrodeposition bath, and the second one is to use a pulse-current (PC) technique [1]. For the former one, during the operation, the composition of additive in the bath decreases so that it is difficult to maintain deposition conditions. On the other hand, the latter one is relatively simple and easy to control an applied current so that it was received a great attention during the last decade (see example in Refs. 2 - 6).

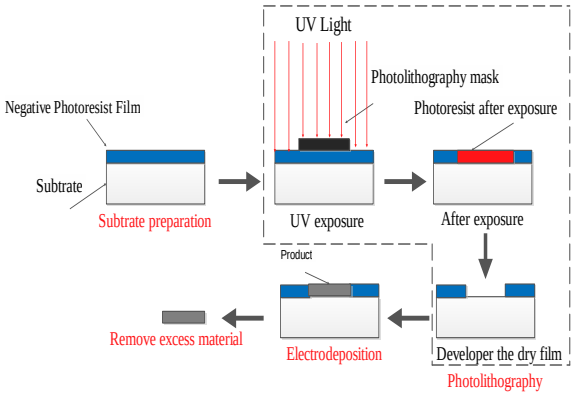
Many researchers have demonstrated that the surface properties of the deposited structure by the PC electrodeposition was better than that by direct current (DC) electrodeposition. It was found that the surface roughness was reduced from 21 to 16.5 nm when the PC frequency increased from 200 to 500 Hz [3]. Xuetao et al. [4] employed different PC parameters, i.e. on-time from 0.1 to 8 ms, off-time from 1 to 30 ms and peak current density from 0.2 to 2 A/cm^2. They reported that the modification of pulse on-time and the peak current density could refine grains and change the preferential orientation of the deposited structure while the increasing of the pulse off-time was good for a crystal growth. Boukhouiete and Creus [5] modified the surface morphology and microstructure with an increasing the pulse off-time from 10 to 100 ms. They reported that the increasing of off-time provoked a refinement of grain size and improved the crystalline quality.

The electrical current is a major cost in the electrodeposition operation, and it is usually reported as a current efficiency [1]. Nasirpouri et al. [2] reported that the PC electrodeposition could improve the current efficiency to 98% while that of DC one was only around 88%.

Despite of an availability of information from the past works, it is difficult or impossible to find an identical study with the same compositions of electrolytes. Therefore, it is necessary to evaluate the PC parameters of a specific electrolyte for any individual work. In this study, we investigated the improvement of the surface roughness and current efficiency obtained in the nickel deposition by comparing between PC and DC electrodeposition using a commercialized nickel sulfate electrolyte. The compositions of this presently employed electrolyte are summarized in Table 1. The surface roughness in a nanoscale was investigated with an AFM technique.

2. Experimental conditions

The fabrication process was summarized in Fig. 1a that consists of a substrate preparation, photolithography and electrodeposition. A substrate was stainless steel with a size of 10 x 4 cm^2 with 3 mm thick. Design of a photolithography mask for patterning the mold is shown in Fig. 1b. It consists of six pieces of micro-actuator and three pieces of square structure for the property tests. The total area of the deposition area is around 5.92 cm^2. The actual workpieces that were deposited are shown in Fig. 1c. Details of the fabrication are explained in the next section.



(a)

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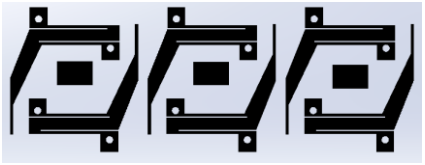


(b)

(c)

Fig. 1 Process flow and deposited nickel structures: (a) UV-LIGA process, (b) patterns on a photolithography mask and (c) deposited nickel structures.

2.1 Substrate preparation

The substrate was cleaned and then polished with a sandpaper with no. 600, 800 and 1200, consecutively. After that, the surface was coated with the photoresist dry-film.

2.2 Photolithography for mold patterning

In this process, the photolithography mask was placed at the middle of substrate, and then exposed to UV light around 30 seconds. The unexposed photoresist dry-film was then removed.

2.3 Electrodeposition of nickel

The nickel was electrodeposited inside the mold. Figure 2a shows the schematic diagram of electroplating instrument. It consists of an electrolyte bath, a KEPCO BOP-36-6m power amplifier, a signal generator (RIGOL DG-2021), hot plate stirrer, a 5-Ω shunt resistor, a magnetic stirring-bar and oscilloscope (AGILENT DSO3062A). Nickel sulfate solution was used as electrolyte, and its compositions are summarized in Table 1.

The square waveform of PC and its on- and off-time are shown in Fig. 2b, and the conditions of PC process are in Table 2. The PC frequency was varied as 10, 50, 200 and 500 Hz at the duty cycle of all cases equal to 50%. The actual current signal that exhibited a fluctuation around 2% is shown in Fig. 2c. The desired thickness for deposition is 0.1 mm. Finally, the deposited substrate was taken into the NaOH bath around 5 minutes to release the deposited nickel structure from the substrate.

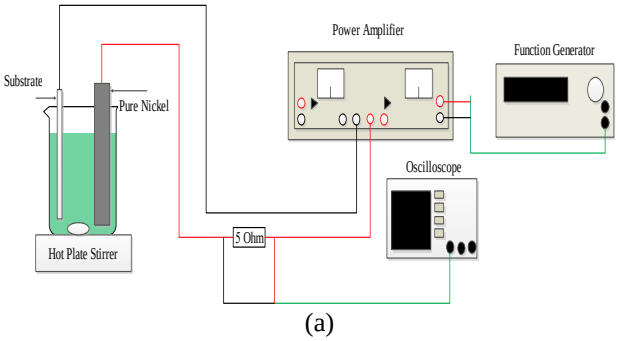
2.4 Sample examination

The surface morphology was observed by a light microscope. At nanoscale, the roughness was measured by an AFM (NanoScope IV). The current efficiency was approximated by comparing a measured weight of three deposited micro-actuators and a theoretical weight.

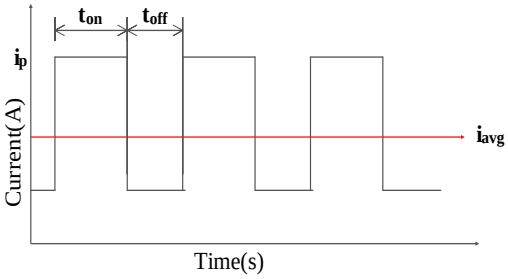
3. Experimental Results

3.1 Surface roughness

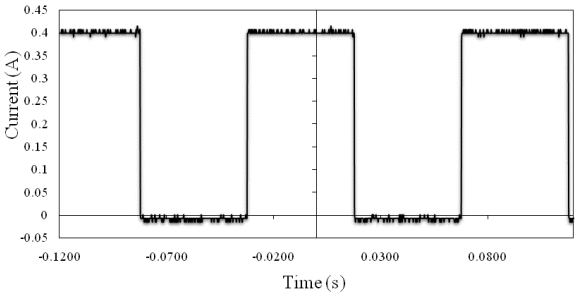
As shown the surface morphology in Figs. 3a-e, the surface roughness of nickel deposited by PC electrodeposition was obviously smaller than that of DC electrodeposition. The comparison of the surface roughness between each case is shown in Figs. 4a-e. The root mean square (rms) roughness of 10 Hz was around 3.5 nm, and only small difference was found among tested PC frequencies. On the other hand, DC electrodeposition provided surface roughness around 11 nm.



(a)



(b)



(c)

Fig. 2 Electrodeposition setup: (a) schematic diagram, (b) square PC signal and (c) actual signal.

3.2 Current efficiency

The current efficiency is defined as the ratio between the actual measured weight and the theoretical weight that could be written as

$$\text{Current Efficiency}(\%) = \frac{W_{measure}}{W_{i_{av},t}} \times 100 \qquad (1)$$

where $W_{i_{av},t}$ is the desired theoretical weight, and $W_{measure}$ is the measured weight from actual deposited workpieces. The chemical reaction at the cathode could be expressed as

$$Ni^{2+} + 2e^{-} \rightarrow Ni \qquad (2)$$

The quantity of metal which obtains at the cathode could be described by using Faraday's law of electrolysis as

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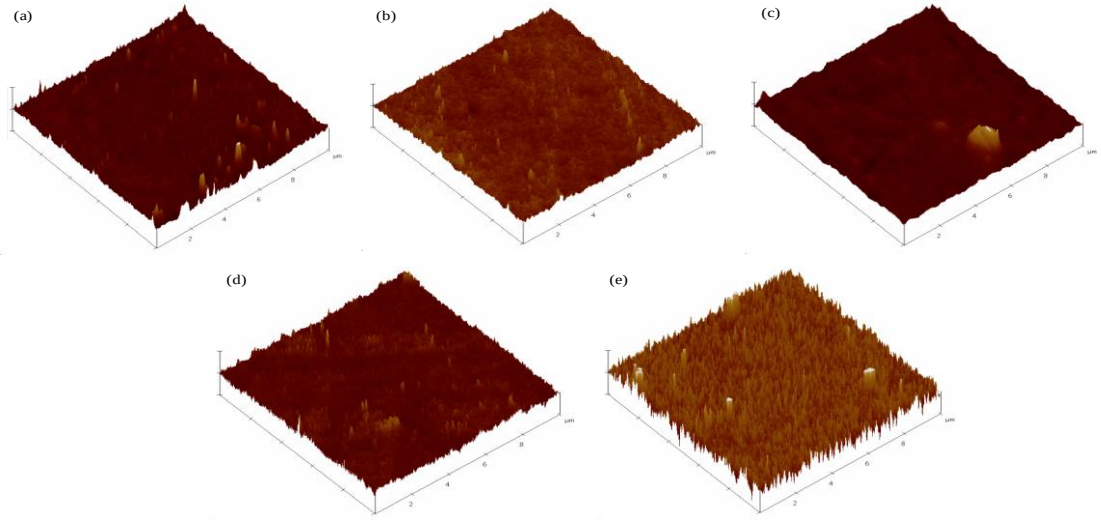

Fig. 3 Surface morphology examined using an AFM technique: (a) 10 Hz, (b) 50 Hz, (c) 200 Hz, (d) 500 Hz and (e) DC electrodeposition.

Table 1 Electrolyte compositions and deposition conditions

Description	Quantity
Nickel Sulfate (g/l)	270
Nickel Chloride (g/l)	75
Boric Acid (g/l)	50
PH	5
Temperature (^{o}C)	43±1
Stirrer speed (rpm)	500

Table 2 Pulse-current electrodeposition parameters

Description	Quantity
Peak current (i_p , mA)	400
Pulse frequency (Hz)	0 (for DC), 10, 50, 200 and 500
t_{on} / t_{off}	1
Avervage current ($i_{av,}$ mA)	200

$$W_{i_{av},t} = \frac{sMI_{av}t}{nF} \qquad (3)$$

where *s* is a molar of oxidized metal at the cathode, *M* is the molecular mass (58.89 g), I_{av} is the average current, *t* is time for deposition, *n* is a number of electron for cathode reaction, *F* is Faraday's constant that equals to 96,485 C. In addition, the theoretical weight of deposition has a relationship with desired thickness as

$$W_{i_{av},t} = \rho_{Ni} A_{Total} h \qquad (4)$$

where A_{Total} is the total area (5.92 cm^2), *h* is the desired deposition thickness (0.1 mm), and ρ_{Ni} is the density of nickel (8.91 g/cm^3). From Eq. 3 and 4, the required deposition time is equal to

$$t = \frac{\rho_{Ni} A_{Total} h}{sMI_{av}} nF \qquad (5)$$

Therefore, the deposition time is two hours and twenty-four minutes for every case.

Figure 5 shows the current efficiency for the electrodeposition obtained by PC technique. At 10 Hz, PC electrodeposition had a current efficiency of 97%. Comparing between PC deposition cases, no significant difference was observed. On the other hand, DC deposition provides the efficiency only around 83%.

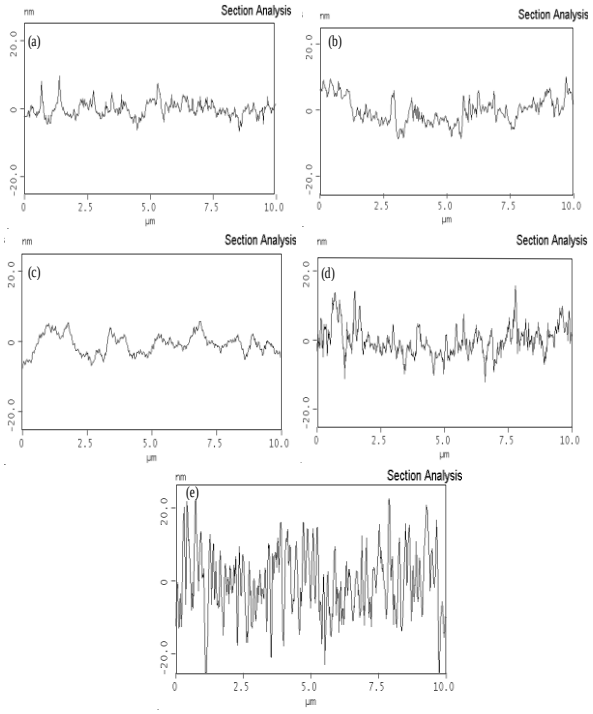

Fig. 4 Roughness profile of PC electrodeposition: (a) 10 Hz, (b) 50 Hz, (c) 200 Hz, (d) 500 Hz comparing to (e) DC electrodeposition using an AFM technique.

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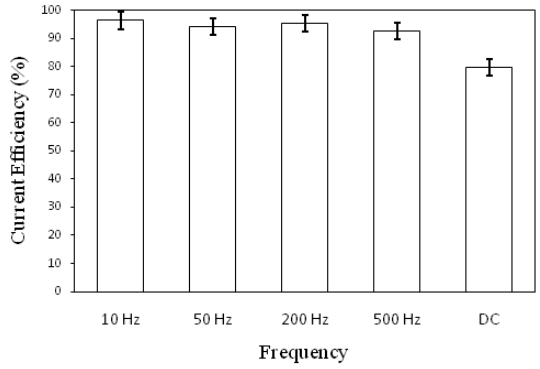

Fig. 5 Current efficiency of PC at different conditions comparing to DC electrodeposition for three independent microactuator workpieces.

From the results, it suggested that the PC electrodeposition could help reducing the surface roughness as well as increasing the current efficiency. In addition, the order of magnitude of obtained data was similar to those in the past works. Among tested PC conditions, the significant difference was not observed; however, the roughness and current efficiency were improved comparing to the DC condition. Regarding the mechanism of the PC deposition that enhances the effectiveness of deposition process, it is a recovery of nickel concentration during off-time interval due to diffusion near a surface of cathode. In contrast, when the metal is deposited with DC technique, the concentration of nickel is depleted and becomes insufficient to make the appropriate chemical reaction [6]. The other reason is about the reduction of hydrogen evolution. During off-time interval, the absorbed hydrogen atoms could escape from the surface of cathode so that the reaction of accumulated hydrogen will not occur or reduce as a result of the recovery of the nickel atom at the surface of cathode as well [3].

4. Conclusion

The improvement of surface roughness and current efficiency of nickel electrodeposition has been performed using nickel sulfate solution with PC deposition. The PC frequency was varied from 10, 50, 200 and 500 Hz, at a fixed duty cycle of 50%, and their properties were compared to those from DC electrodeposition. The surface roughness of the deposited nickel surface was around 3.5 nm while the current efficiency was around 97% at the PC frequency of 10 Hz. When increasing the PC frequency, the roughness and current efficiency were not significantly different. However, they were much improved comparing to those of DC deposition.

5. Acknowledgement

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6. Reference

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