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The Influence of Surfactant CTAB on the Microstructure and Material Properties of Nickel Microelectroforming

Yann Cheng Chen[1], Sheng Lung Kuo[2,a], Jou Long Lee[3], Shie Tsung Ke[1], Chia Hao Wong[2] and Ming Der Ger[1,b]

[1] Department of Applied Chemistry & Materials Science, Chung-Cheng Institute of Technology, National Defense University, Tao-Yuan, Taiwan, ROC

[2] Institute of Materials and Chemical Engineering, National Chin-Yi Institute of Technology, Taichung, Taiwan, ROC

[3] Department of Chemical & Materials Engineering, Lung Hwa University of Science and Technology, Tao-Yuan, Taiwan, ROC

[a]kuosl@chinyi.ncit.edu.tw, [b]mdger@ccit.edu.tw

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Abstract. The influence of surfactant CTAB (cetyl trimethyl ammonium bromide) on electro-deposited nickel layer has been investigated in this research. Our result shows that CTAB added in the electrolysis bath can effectively remove the hydrogen to obtain a smoother nickel layer. The effect of CTAB on the surface roughness is also significant. It may be ascribed to the adsorption of CTAB on the electrode surface which results in a hindering effect in the electrodeposition process. Increasing the concentration of CTAB, the grain size of nickel deposit was reduced and the micro-hardness of the nickel deposit was therefore improved. The hardness of the metal layer can be promoted to 450 Hv when 300 ppm CTAB is added.

Introduction

Many researchers have published the use of LIGA technology in the micro-electric-mechanical system (MEMS) since 1960s. One famous development is from the Thomas J. Watson Research Center of IBM Corporation, which created the technology of lithography to manufacture the copper micro-conduit from the LIGA electrolysis technology in 1965.

Nickel has been widely used as an important industrial material because of its excellent properties in physical, mechanical, and chemical aspects. It is generally considered as a reductive metal to restrain the corrosion of substrate. In addition, the reduction of nickel ion can be aided by adding the surfactant in the electrolysis bath to wet the substrate surface. There is some literature discussing the effect of surfactant in the nickel electrolysis bath on the deposited nickel layer in the past [1-5].

Surfactants usually play an important role in the electrolysis process to bring some properties of the electro-deposited layer, such as the brightness, moistness, smoothness, and homogeneity. The surfactant CTAB (cetyl trimethyl ammonium bromide) is a cationic surfactant. It was considered as having good potential in the application of nano-technology because of its strong adsorbed ability in nano particles [6-8]. Besides, the CTAB is also suitable for being as a corrosion inhibitor [9-11]. However, using CTAB in the deposition research of high aspect-ratio LIGA system has rarely been explored. Generally, the hydrogen gas will generate in the LIGA process. Since the hydrogen gas is generated on the cathodic surface, the deposition of metal layer on the electrode surface will be hindered in the LIGA system. Moreover, if the hydrogen bubbles fill the microchannels, the electrodeposition process will be interrupted in this micro-system process. The surfactant can decrease the adhesion of hydrogen bubbles, and therefore keeps the procedure going on and gets a smoother deposited metal layer in the LIGA process.

In this work, we aim at developing a high quality nickel electrodeposited layer. The influence of surfactant CTAB on the nickel electro-deposited layer has been investigated. The microstructures and material properties of the nickel deposits were also discussed.

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Experimental

The nickel sulfamate bath was used as plating electrolyte in this study. The bath composition and ranges of experimental parameters are shown in Table 1. The copper plate was used as the electrode. The conditions of the electrochemical experiment were operated with current density of 5 A/dm^2, temperature of 50°C and pH value ranged from 3.8 to 4.0. Table 2 shows the designation of the Ni deposited in different electroplating bath.

The corrosion resistance of the nickel deposit was tested by potential stat (EG&G) and Electrochemical Impedance Spectroscopy (EIS) in 3.5% NaCl solution. The morphology of the electrodeposition layer was observed using both SEM and AFM instruments. The micro-hardness of the electrodeposition layer was tested using a Vickers diamond indenter at a 100 g load. Finally, the structure of the electrodeposition layer was analyzed by XRD with 5°/min scan rate and scanning angle from 0° to 100° (2 θ).

Table 1. Chemical composition and operation condition of the electrolyte

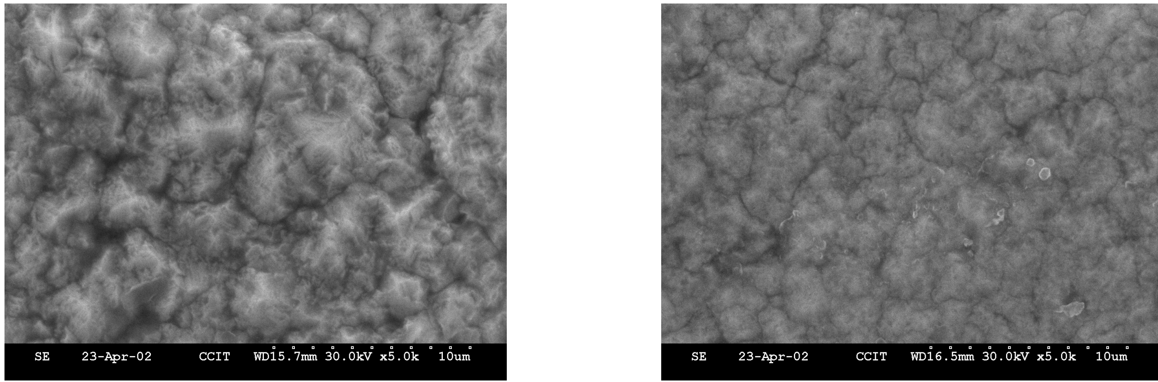
Component	Condition
Nickel sulfamate	320 [g/L]
Nickel chloride	10 [g/L]
Boric acid	40 [g/L]
CTAB	10 ~ 300 [ppm]
Current density	5 [A/dm^2]
Temperature	50 [℃]
pH	3.8 ~ 4.0

Table 2. Designation of the Ni deposited in different electroplating bath

Symbol	Composition
Ni-0	Pure Ni bath (without CTAB)
Ni-10	Ni + 10 [ppm] CTAB bath
Ni-100	Ni + 100 [ppm] CTAB bath
Ni-300	Ni + 300 [ppm] CTAB bath

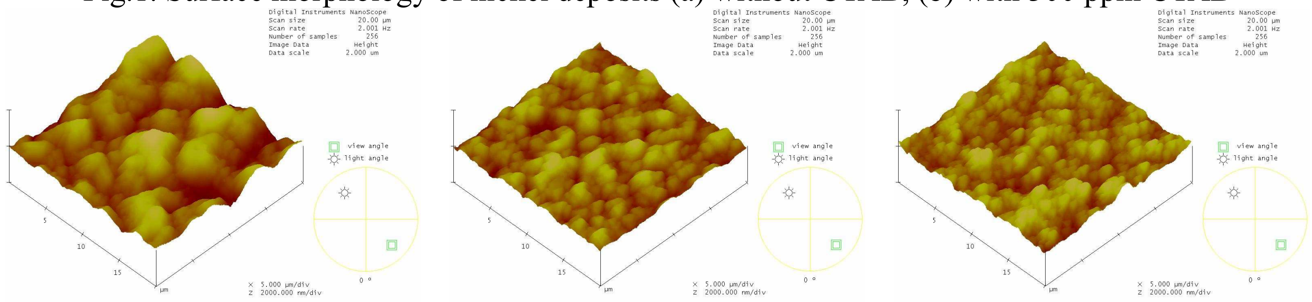
Results and discussion

Figure 1 shows the surface morphology of nickel deposits at different concentrations of surfactant (CTAB) in the electroplating bath. It appears the surface morphology of the Ni deposit obtained with 300 ppm CTAB is smoother than that of Ni deposit obtained without the surfactant. Furthermore, Figure 2 shows the 3-D AFM diagram of Ni deposit made with different concentration of CTAB in the electroplating bath. It is found that the roughness reduced with an increase of CTAB concentration. The effect of surfactant CTAB on the surface roughness is significant. It might be ascribe to the adsorption of CTAB on the electrode surface resulting in a hindering effect in the electrodeposition process. The growth rate of the nickel deposit was depressed in the deposition. Thus, a fine and uniform crystal structure was obtained.



(a) Ni-0 ppm CTAB (b) Ni-300 ppm CTAB

Fig.1. Surface morphology of nickel deposits (a) without CTAB, (b) with 300 ppm CTAB



(a) Ni-0 ppm CTAB (b) Ni-100 ppm CTAB (c) Ni-300 ppm CTAB

Fig.2. 3-D AFM diagram of Ni deposits (a) Pure Ni, (b) Ni-100, (c) Ni-300

Figure 3 shows the variation of overpotential in the electrodeposition process for the various concentration of surfactant. The overpotential was at 1.3 V under the original electroplating bath. Then, the overpotential was raised from 1.7 V to 2.1 V as the concentration of adding CTAB was increased from 100 ppm to 300 ppm, respectively.

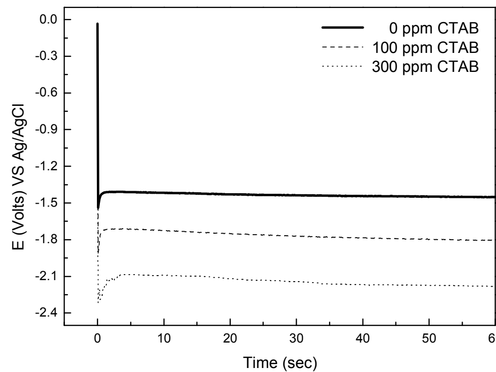


Fig.3. Variation of overpotential in deposition process for various CTAB concentrations.

The micro-hardness of nickel deposit is influenced directly by the crystal structure of nickel layer. Figure 4 shows the results of the hardness of nickel layer deposited with different concentration of CTAB. The hardness of the nickel deposit is linearly increasing with the increase of the CTAB concentration in the electroplating bath. The hardness of the nickel metal layer is 450 Hv at the concentration t of 300 ppm CTAB in the electroplating bath. Increasing the CTAB concentration, nickel deposit would therefore reduce the grain size of structure leading to improvement of the micro-hardness. The XRD diffraction shown on Figure 5 indicates that the microstructures of nickel deposit depend on the concentration of CTAB in the electroplating bath. Especially, the intensity of Ni(111) peak increases abruptly at the concentration of 300 ppm CTAB.

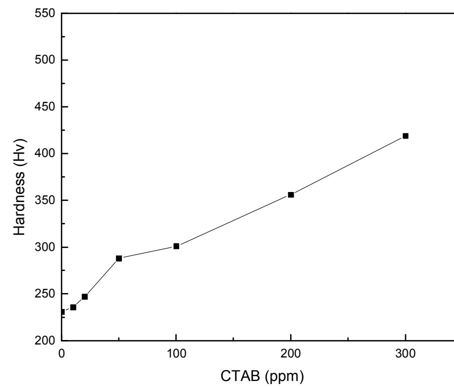


Fig.4. Hardness variation of Ni deposits for various CTAB concentrations.

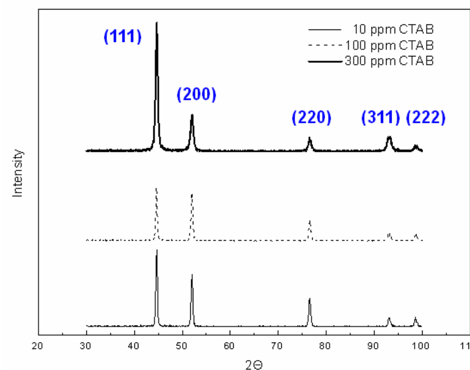


Fig.5. X-ray diffraction patterns of Ni deposit with different electroplating bath.

Figure 6 shows the polarization curve of the corrosion test of nickel deposit in the 3.5 % NaCl solution. The corrosion potential (E_{corr}) of the corrosion resistance test shifts from -109 mV to -371 mV for the nickel deposit under the addition of CTAB in the electroplating bath. The corrosion current (I_{corr}) of the test is corresponding from 1.94×10^{-6} A/cm^2 to 1.40×10^{-5} A/cm^2. Although the corrosion resistance of nickel deposit decreases with the increase of the CTAB in the electroplating bath, there was an obvious passivation region occurring (point of arrow A) in the Ni-300ppm CTAB system. This appearance may be explained with the mechanism that the surfactants embedded in the nickel deposit would disassociate and adsorb on the surface to inhibit the corrosion reaction.

Figure 7 shows the Nyquist diagram of nickel deposit in the 3.5% NaCl solution. The corrosion resistance of Ni-100 and Ni-300 is worse than that of the Ni-0. However, the corrosion resistance of Ni-300 has the phenomena of Warburg corrosion resistance. It may be presumed that the deposit of Ni-300 surface was covered with a passive film resulting in Warburg effect. This corrosion result has same tendency with that obtained by polarization curve.

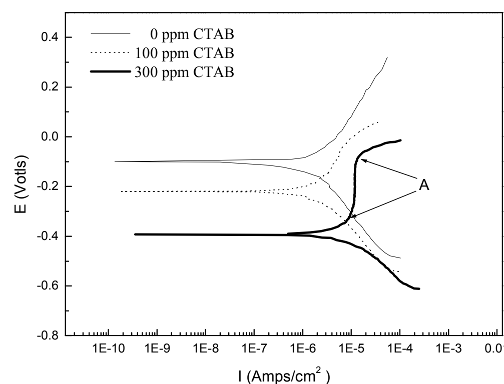


Fig.6. Polarization curve of Ni deposits with different electroplating bath

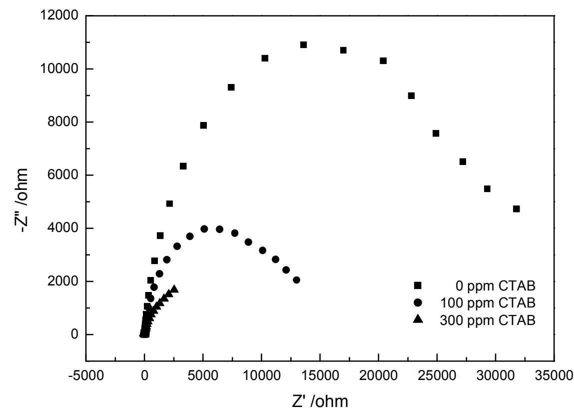


Fig.7. Nyquist plots of Ni deposits with different electroplating bath

Conclusions

1. The effect of surfactant CTAB on the surface roughness of nickel deposit is significant. It is found that the roughness reduced with an increase of CTAB concentration.

2. The hardness of the nickel layer is increased with the added concentration of CTAB in the electrolysis solution. The hardness of deposited nickel layer can be promoted to 450 Hv at the amount of 300 ppm CTAB.

3. Although the corrosion resistance of nickel deposit decreases with the increase of the CTAB in the electroplating bath, there is an obvious passivation region occurred in the Ni-300ppm CTAB system.

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