



# A comparative study on 2-Aminoethanethiol and L-Cysteine as new additives for electroforming nickel mesh

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## ABSTRACT

Electroforming of nickel mesh was performed in bath with different concentration of 2-Aminoethanethiol and L-Cysteine to achieve a higher aspect ratio. Although 2-Aminoethanethiol and L-Cysteine have a similar part in their molecules, the optical observation on the cross section of mesh indicated that 2-Aminoethanethiol was an effective additive in improving the aspect ratio of nickel printing mesh whereas L-Cysteine was not. Electrochemical behaviors of 2-Aminoethanethiol and L-Cysteine in the electroforming bath were further evaluated by linear sweep voltammetry (LSV) and galvanostatic measurements using rotating disk electrode (RDE). Both 2-Aminoethanethiol and L-Cysteine could effectively reduce the cathodic polarization and promote deposition of nickel ions. The depolarization effect of 2-Aminoethanethiol which associated with convection is stronger in the high diffusion region than that in the low diffusion region in the present potential region. However, the depolarization effect of L-Cysteine which also associated with the convection is stronger in the low diffusion region than in the high diffusion region unless the potential is negative enough. The different depolarization behaviors under different convection conditions made significant influence on the deposition of nickel ions on the board surface and the internal surface, which finally leads to the high aspect ratio.

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## 1. Introduction

Electroformed nickel mesh [1,2] has been used to get the preset patterns in printing and dyeing industry for a long period. Dyes selectively ooze out of the microvia of mesh during the printing process to print the images. Hence, the mesh number and ratio of opening microvia area to the whole surface area play an important role in getting fine patterns [3,4]. As well known, current density is the essential factor to the deposition of nickel ions. However, the current density distribution varies in different positions due to the strong influence of the shape of surface. The uneven current density leads to the unsynchronized growth rate of nickel at different position and even closure of the microvia [5,6], subsequently degrades the printing fineness. With the increase of thickness, the diameter of microvia decreased dramatically. Although mesh with small thickness definitely possess large microvia diameter for the

flow of dyes but the thinner thickness always means poor reserves for dyes. Thus, to increase the diameter of microvia while keep the ideal thickness become the pivotal issue for the electroforming of mesh. Aspect ratio of mesh (the ratio of growth of thickness to the reduction of microvia diameter) is introduced to quantify the growth ratio along the two directions and evaluate the fineness of mesh. The aspect ratio clearly reflects the growth on different position, and it urgent to find out an effect method to control the reduction and deposition of ions at the different positions.

Generally, the cove shape mesh always results in the decreased current density on inner surface of microvia, comparing with current density on the board surface especially on the sharp edge near the “mouth” of microvia [7,8]. The aspect ratio decreased by this current density distribution. However, the shape-related current density distribution that affects the reduction of nickel ions could not be easily changed by tailoring the shape of substrate microvia for most of industrial cases. Another way to control reduction of ions is adding additives to affect the electron transfer through the adsorption of organic molecule with nickel ions and with substrate [9–11]. Until now, only few additives have been investigated deeply.

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Xiao et al. [12] studied the synergistic effect between a Triblock copolymer and chloride ions, they proposed that Triblock copolymer and chloride ions could form a continuous barrier film on the board surface to inhibit deposition of metal ions. Chen et al. [13] studied the effects of supporting electrolytes ( $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ) on microvia electroforming, their study suggested that supporting electrolytes could affect surface coverage of the suppressor (Tetranitroblue tetrazolium chloride, TNBT) on metal surface, so as to achieved the purpose of controlling metal deposition. In addition, it has been evidenced by researchers that the forced convection has greatly effect on the mass transfer in the electroplating bath [14,15] and the adsorption of organic additives. Lu et al. [16] studied the additives including accelerator (bis (3-sulfopropyl) disulfide, SPS), inhibitor (EPE), and leveler (Janus Green B, JGB), and found that additives at different rate of mass transfer affected the deposition potential of metal ions on the substrate surface, thus affected the electrodeposition of metal ions at different locations of the substrate. Although there are some reports on the electrodeposition of copper under different convection and potential conditions, the relative mechanism investigation is inadequate to address and predict the electroforming of nickel microvia on the purpose of improving aspect ratio.

Herein, the electroformed nickel mesh was prepared when 2-Aminoethanethiol and L-Cysteine were used as the additives at the same condition. The effects of 2-Aminoethanethiol and L-Cysteine on the electroforming of nickel mesh were studied, mainly focused on the diameter of microvia and aspect ratio of nickel mesh. The electrochemical behaviors of 2-Aminoethanethiol and L-Cysteine were then characterized by linear sweep voltammetry and galvanostatic measurements with rotating disk electrode (RDE) to simulate the deposition on the board surface of nickel mesh and inner surface of microvia.

## 2. Experimental

### 2.1. Electroforming of nickel mesh

The size of substrate mesh used for nickel mesh electroforming experiments was  $40\text{ mm} \times 35\text{ mm} \times 0.029\text{ mm}$ . The microvia density was 49 per cm. The shape and dimension of microvia is shown in Fig. 1. A sulfur-containing (0.01–0.15 wt%) nickel plate with size of  $4.5\text{ cm} \times 5\text{ cm} \times 1\text{ mm}$  was used as the anode. The nickel mesh specimen was plated at a current density of  $10\text{ A/dm}^2$  for 20 min in 250 ml plating solution. The temperature of the plating solution was  $40^\circ\text{C}$ . Constant agitation was performed by magneton with rate of 100 rpm during electroforming. An optical microscope (OM, MIE 2.0) was used to observe the cross-sectional images of microvia

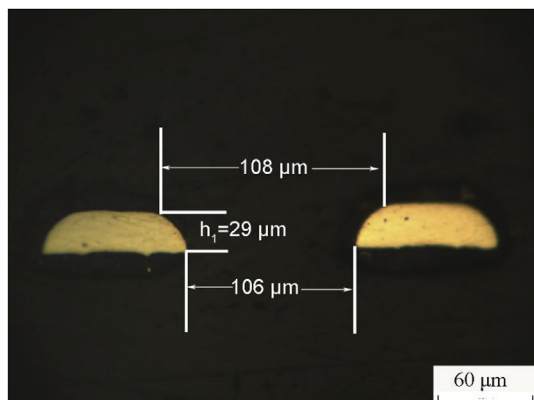


Fig. 1. OM images of microvia cross-section before electroforming.

and measure the diameter of microvia.

The composition of base electrolyte used for all plating experiments was composed of 150 g/L  $\text{NiSO}_4$ , 40 g/L  $\text{NiCl}_2$ , 35 g/L  $\text{H}_3\text{BO}_3$ , 0.28 g/L 1,4-butyndiol, and 0.1 g/L Sodium dodecyl sulfate. Furthermore, the additives employed in this work were 2-Aminoethanethiol and L-Cysteine, the molecular structure of which are shown in Fig. 2. They were added into the base electrolyte through dilution from stock solution prepared with proper contents.

### 2.2. Electrochemical characterization

All of the electrochemical tests were performed in a three-electrode cell using a PARSTAT 3000 electrochemical working station. The volume of the tested electrolyte was 100 ml and the temperature of tested electrolyte was maintained at the same value with the electroforming experiment. A platinum rotating disk electrode (Pt-RDE) with a diameter of 5 mm was used as the working electrode. Before each electrochemical measurement, a thin nickel layer with a thickness of 500 nm was pre-deposited onto the Pt-RDE in the base electrolyte to prepare a Ni-RDE, a platinum plate was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The potentials given in this study were all respect to SCE. The LSV polarization plots [17,18] were collected with a negative-going sweep from 1.0 V to  $-0.8\text{ V vs. SCE}$  at a scan rate of  $0.5\text{ mV/s}$ . Galvanostatic measurements (GMs) [19,20] were performed to analyze the effects of additives on cathodic polarization of electrolyte for nickel electrodeposition. GMs experiments were carried out at the current density was fixed at  $2\text{ A/dm}^2$ . In order to investigate the effects of 2-Aminoethanethiol and L-Cysteine on the electrodeposition of nickel ions on the board surface of nickel mesh and on the inner surface of microvia, 100 rpm and 1500 rpm of rotation speed were applied to simulate the convection respectively [21,22].

## 3. Results and discussion

### 3.1. Influence of 2-Aminoethanethiol and L-Cysteine in nickel mesh electroforming

The cross-sectional morphologies of nickel mesh prepared with 2-Aminoethanethiol are shown in Fig. 3. After the electroforming, the microvia size of mesh without 2-Aminoethanethiol reduced from  $106\text{ }\mu\text{m}$  (in Fig. 1) to  $73\text{ }\mu\text{m}$  and the thickness of microvia wall increased by  $33\text{ }\mu\text{m}$ , as shown in Fig. 3a. The microvia size of mesh prepared with  $1\text{ mg/L}$  2-Aminoethanethiol reduced from  $106\text{ }\mu\text{m}$  to  $81\text{ }\mu\text{m}$  and the thickness of microvia wall increased by  $25\text{ }\mu\text{m}$  as shown in Fig. 3b. The results strongly suggested that 2-Aminoethanethiol had an inhibiting effect on the growth on the inner surface. When the 2-Aminoethanethiol concentration was increased from 0 to  $5\text{ mg/L}$ , the size of diameter increased correspondingly as shown in Fig. 3a–d. However, it could be found that the size of diameter decreased with the 2-Aminoethanethiol concentration further increased from 5 to  $20\text{ mg/L}$  as shown in

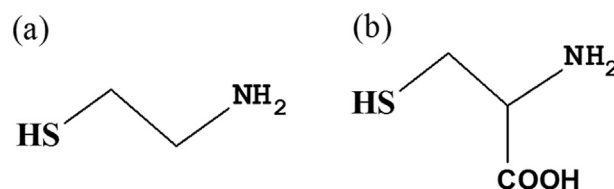


Fig. 2. (a) Molecular structures of 2-Aminoethanethiol and (b) molecular structures of L-Cysteine.

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