Effect of sulfuric acid concentration on the quality of copper microcolumns in localized electrochemical deposition

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Abstract

Localized electrochemical deposition (LECD) is a promising method for three-dimensional micro-/nanofabrication and, thus, the factors influencing LECD have been intensively investigated. This study examined the effect of sulfuric acid concentration on copper microcolumns deposited by LECD using a microanode with a diameter of 20 μm. With 0.05 mol l⁻¹ sulfuric acid, the deposition voltage of the optimal deposited morphology of copper microcolumns was at 2.9 V, but the column diameter was larger than the anode diameter. With 0.5 and 2.0 mol l⁻¹ sulfuric acid, the optimal deposited morphology of copper microcolumns were at 3.2 V and 3.4 V, respectively, but the diameters of the copper microcolumns were smaller than the anode diameter. In the LECD process, the deposition rate is proportional to the deposition voltage. Because of the hydrogen evolution, the deposition rates of copper microcolumns at high sulfuric acid concentration were lower than those at low and medium sulfuric acid concentrations. The results of this study indicated that the deposition rate obtained the optimal surface topography was 0.22 to 0.327 μm s⁻¹, which had reference significance to improve the quality of the copper microcolumns. The effect of sulfuric acid on the LECD was demonstrated using a competitive reduction mechanism.

1. Introduction

In micro-/nanomanufacturing, electrochemical methods are increasingly used to deposit three-dimensional (3D) micro-/nano scale metal structures. For this purpose, localized electrochemical deposition (LECD) is a very promising method. Since LECD was first proposed by Madden et al in 1996 [1], various 3D microstructures, including high-aspect-ratio copper columns, springs, Cu–Ni alloy columns, copper walls, and other complex shapes, have been fabricated by LECD [1–4].

Most LECD studies have focused on Cu or Ni columns. In addition to establishing growth models [5] and numerical simulations [6] for column deposition, various parameters, including the electric field distribution between electrodes, the pulse power, the deposition voltage, the deposition gap, the deposition direction (horizontal or vertical) of the anode, and the contact mode (intermittent or continuous) of the anode [7–12], have been investigated. This work, which provided an understanding of how specific factors affect the surface morphology, column diameter, and structural characteristics, has laid the foundation for the practical application of LECD. For instance, Wang et al deposited copper walls through the layer-by-layer movement of a microanode [3], whereas Yeo and Choo deposited hollow cylinders through the rotation of a microanode [13]. Furthermore, Habib et al used an array mask to fabricate multiple electrodes simultaneously by LECD [4].

In addition to the above-mentioned basic research, the effect of additives on LECD has also attracted considerable attention. Bis-(3-sulfopropyl) disulfide and chloride ions have been found to increase the deposition rate of copper ions at low voltages to improve the surface quality of copper columns [14]. Furthermore, saccharin and saccharin sodium have been added to electrolytes to reduce the porosity and surface roughness of microcolumns [2, 15]. However, the strong electric field between the electrodes may cause decomposition or rearrangement of organic additives. Therefore, the applicability of additives in LECD is severely limited. However, sulfuric acid is often added to the electrolyte during copper electrodeposition because
the pH can influence the form in which copper ions exist in copper sulfate aqueous solution [16]. Moreover, Danilov et al. as well as Grujicic and Pesic have conducted detailed studies on the effect of pH in the range of 0.3 to 4 on copper electrocrystallization. An increase of pH produces nuclei with a coarser texture and lower population density, and increase the deposition rate of copper ions [17, 18]. Further, Shin and Liu deposited porous foam copper by using hydrogen bubbles that adhered to the cathode surface at a high sulfuric acid concentration [19]. The formation of bubbles between the electrodes has been observed using x-ray microradiography [20] and a high-speed camera [21]. Besides, little research has been conducted on the effects of bubbles on the LECD process. Therefore, a better understanding of the effect of sulfuric acid on copper electrodeposition by LECD is required.

In this study, the effects of the sulfuric acid concentration on the surface morphology and diameter of copper microcolumns were investigated. In addition, the deposition voltage and deposition rate under different sulfuric acid concentrations were examined. Based on the experimental results, a competitive reduction mechanism for the effect of sulfuric acid was deduced.

2. Experimental procedure

The photograph of the experimental equipment used for LECD was shown in figure 1. The equipment was mainly composed of the anode, sedimentation tank containing cathode, 3D control platform (PI M-L01; the setting of rate: 1 μm per step), DC power, control software and control PC. In LECD, the anode has the greatest impact on the deposition process. The anode was fabricated by high borosilicate glass tube (HBGT; inner diameter: 0.2 mm) with Pt wire (diameter: 20 μm) placed in an alcohol lamp to be drawn out rapidly, and then polished with an EG-401 microgrinder (Narishige Co., Ltd) to expose the end of the Pt wire and reduce the thickness of the HBGT, as shown in figure 2. The cathode was consisted of a round copper plate (diameter: 15 mm, thickness: 0.5 mm) mounted using epoxy resin. During the LECD experiment, the anode was connected to the positive pole of the power supply via a wire, and the other end of the anode was immersed in the electrolyte for electrodeposition. Similarly, the cathode fixed in the deposition tank was connected to the negative pole of the power supply by a wire. The electrolytes were composed of 0.8 mol l⁻¹ copper sulfate (CuSO₄·5H₂O) and 0.05, 0.5, or 2.0 mol l⁻¹ sulfuric acid (H₂SO₄).

Before the electroplating deposition of the copper column, the initial deposited position of the anode fixed on the 3D control platform was set by the contact current exceeding the threshold (0.1 A) at a DC voltage of 2.8 V when the anode was moved towards cathode at a high resolution of 1 μm per step. At this time, the DC power was turned off. Then the required electrolyte was poured into the tank, meanwhile some parameters, including the deposition DC voltage value and the deposition gap (e.g., 5 μm), were set by the software to start the deposition. Figures 3(a)–(d) depicted the step-by-step deposition manner of the copper column. The copper column grew towards to the anode under the DC voltage until their contact caused the current rose instantaneously above the threshold current, which indicated that a deposition gap was completed and the next gap was triggered. Subsequently, the DC power was turned off and the deposition was paused. After the anode was moved up the predefined gap (5 μm) at a rate of 1 μm per step in the vertical direction, the DC power was turned on to continue the deposition of the copper column. This process was repeated until the copper column deposition height (1000 μm) was reached.
3. Results and discussion

3.1. Copper column deposition at a low sulfuric acid concentration (0.05 mol l\(^{-1}\))

Scanning electron microscopy (SEM) images of the copper microcolumns deposited in the presence of 0.05 mol l\(^{-1}\) sulfuric acid are shown in figure 4. The deposition voltage had an impact on the quality of the deposited copper column. In the case of 2.8 V, the average diameter of the copper microcolumn was 76.5 \(\mu\)m, and the large grains on the surface of the copper column resulted in a rough surface (figure 4(a)). In the case of 2.9 V, the copper microcolumn diameter decreased to 44.7 \(\mu\)m, and the grains on the surface became smaller, resulting in a smooth surface (figure 4(b)). Increasing the deposition voltage to 3.0 V decreased the copper microcolumn diameter to 22.7 \(\mu\)m, while bumps appeared on the trunk and top of the column, as shown in figure 4(c). Further increasing the deposition voltage to 3.2 and 3.4 V resulted in the branches and bumps becoming more obvious, and the deposited structure was no longer a microcylinder (figures 4(d) and (e)). The copper microcolumn diameters obtained by LECD in 0.05 mol l\(^{-1}\) sulfuric acid are summarized in figure 5(a).

The voltage was a key factor that influenced the surface morphology and diameter of copper column. As the voltage increased, the stronger electric field between electrodes accelerated the migration of copper ions to the cathode deposition. Thus, the deposition rate of the copper was proportional to the voltage in 0.05 mol l\(^{-1}\) sulfuric acid (figure 5(b)). Because the deposition rate influences the formation and growth of the crystal nuclei [16, 22], resulting in the morphology change from rough to smooth, then from smooth to bump and branch as increasing deposition voltage. Due to the influence of the bump structure, the diameter of the copper microcolumn was increased at 3.2 V. Although the optimal surface morphology of copper microcolumns obtained from 0.05 mol l\(^{-1}\) sulfuric acid in figure 4 was deposited at 2.9 V, the microcolumn diameter was larger than the anode diameter and the top was uneven.

Figure 2. Optical microscope image of anode.

Figure 3. Schematic of control gap deposition process for LECD: (a)–(d).
3.2. Copper column deposition at a medium sulfuric acid concentration (0.5 mol l\(^{-1}\))

Figure 6 depicts SEM images of the copper columns deposited in the presence of 0.5 mol l\(^{-1}\) sulfuric acid. At a voltage of 3.0 V, the copper microcolumn diameter was 14.6 \(\mu\)m and the grain size was small, but the surface was not very smooth (figure 6(a)). However, at a voltage of 3.2 V, the copper microcolumn diameter was 14.1 \(\mu\)m, the grains were very fine, and the surface was smooth, as shown in figure 6(b). Although increasing the deposition voltage to 3.4 V decreased the diameter of the copper microcolumn to 13.5 \(\mu\)m, bump structure...
started to grow and the surface morphology became poor (figure 6(c)). Further increasing the deposition voltage resulted in an obvious bump structure at 3.6 V (figure 6(d)) and a branched structure at 3.8 V (figure 6(e)).

As the sulfuric acid concentration increased, the more H\(^+\) reduction could suppress the copper deposition rate to improve the bump and branch structure on the copper column surface. Thereby, the influence of the hollow structure caused the diameter of copper microcolumn to increase at 3.8 V with 0.5 mol l\(^{-1}\) sulfuric acid in figure 5(a). Compared with the quality and deposition rate of microcolumns of 0.05 mol l\(^{-1}\) sulfuric acid, it was found that the diameter of the obtained copper microcolumn was smaller at same deposition voltage in figure 5(a), the deposition rate was slower in figure 5(b) and the surface morphology of figures 6(a)–(c) became better than the morphology of figures 4(c)–(e). In the deposition experiment, the voltage had exceeded the reduction potential of H\(^+\) and Cu\(^{2+}\). Because of competitive reaction, the total charge of the cathode is the sum of the reduction charges of H\(^+\) and Cu\(^{2+}\). Thus, increasing the sulfuric acid concentration from 0.05 mol to 0.5 mol enhanced the degree of hydrogen ion competition reaction to inhibit the deposition rate of copper, which improved the quality of the surface and decrease the microcolumn diameter at high voltage. Meanwhile, the deposition threshold voltage also was increased from 2.8 V to 3.0 V.

3.3. Copper column deposition at a high sulfuric acid concentration (2.0 mol l\(^{-1}\))

Figure 7 depicts SEM images of the copper microcolumns deposited at different voltages in the presence of 2.0 mol l\(^{-1}\) sulfuric acid. At 3.4 V, the surface of the copper column had small crystal grains and the column diameter was 14.5 \(\mu\)m, as shown in figure 7(a). At 3.6 V, the copper microcolumn diameter decreased to 11.5 \(\mu\)m and the grain size was very fine, but bumps were observed on the smooth surface (figure 7(b)). Further increasing the deposition voltage to 3.8, 4.0, and 4.2 V gave copper microcolumns with diameters of 9.9, 10.4, and 18.9 \(\mu\)m, respectively. Owing to the formation of bumps and branches on the surface, the morphologies of these structures became increasingly worse (figures 7(c)–(e)). Thereby, the influence of the hollow structure caused the diameter of copper microcolumn to increase at 4.2 V in figure 5(a).
In the presence of 2.0 mol l\(^{-1}\) sulfuric acid, the threshold voltage was already 3.4 V. Because a lot of hydrogen bubbles generated by the hydrogen evolution reaction at a voltage below 3.4 V could interrupt the deposition of copper in the LECD process. Compared with the other deposited at 3.4 V, the copper deposition rate of 2.0 mol l\(^{-1}\) sulfuric acid was the slowest in figure 5(b). However, the inhibited copper deposition rate of 2.0 mol l\(^{-1}\) sulfuric acid was beneficial to the rapid formation and the slow growth of copper crystal nuclei to obtain no bump and branchless copper microcolumn. The optimum deposition voltages of the optimal deposition morphology obtained at different sulfuric acid were 2.9, 3.2, and 3.4 V, respectively. It indicated that the deposition rate in the range of 0.22 to 0.327 \(\text{um s}^{-1}\) was beneficial to improve the deposition quality of copper microcolumn.

### 3.4. Mechanism of the sulfuric acid effect on copper microcolumn deposition

In local electrochemical deposition, the electrochemical reactions occurring on the cathode and the anode were shown in equations (1)–(3).

**Anode:**

\[
2\text{H}_2\text{O} = 4\text{H}^+ + \text{O}_2 + 4\text{e}^-
\]  

**Cathode:**

\[
\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}
\]  

\[
2\text{H}^+ + 2\text{e}^- = \text{H}_2
\]

The number of hydrogen ions and copper ions involved in the reaction at the cathode could be calculated. The calculation formula was shown in equations (4)–(7).
The copper column diameter can be reduced by up to 50% by the effect of the increasing voltage, the electrode polarization and the electric field. Due to the influence of the branched structure and the bump structure, it was only calculated the reacted molar ratio of hydrogen ions to copper ions on the cathode could be represented by equation (7).

\[ \frac{n_{H^+}}{n_{Cu^{2+}}} = \frac{2 \times i_{H^+}}{i_{Cu^{2+}}} \]

where \( i_{H^+} \) is the current of hydrogen ion reaction, \( i_{Cu^{2+}} \) is the current of copper ion reaction in A, the average line current \( i \) is the sum of \( i_{H^+} \) and \( i_{Cu^{2+}} \), \( \rho \) is the density of copper in g m\(^{-3}\), \( V \) is the average deposition rate in \( \mu m \) s\(^{-1}\), \( i \) is the diameter of the copper microcolumn in figure 5(a), \( t \) is the time, \( \pi \) is 3.14, \( F \) is Faraday’s constant, \( z \) is the charge, \( M \) is molar mass of copper in g.

According to the deposition rate and diameter in figure 5, the deposition mass of the copper microcolumn per unit time could be calculated by equation (4). Then the reaction charge of copper ions could be calculated by equation (5) according to Faraday’s law. The current \( i \) was recorded by the control software, as shown in table 1. Meanwhile, \( i_{Cu} \) could be represented by equation (6).

Thus, the molar ratio of participating hydrogen ions to copper ions on the cathode could be represented by equation (7).

\[ \frac{n_{H^+}}{n_{Cu^{2+}}} = \frac{2 \times i_{H^+}}{i_{Cu^{2+}}} \]

Due to the influence of the branched structure and the bump structure, it was only calculated the reacted molar ratio of hydrogen ions to copper ions (\( n_{H^+}/n_{Cu^{2+}} \)) of the deposited copper cylinder, as shown in table 1. Compared to three sulfuric acids, the \( n_{H^+}/n_{Cu^{2+}} \) increased with the increasing sulfuric acid concentration. With 0.05 mol l\(^{-1}\) sulfuric acid, the \( n_{H^+}/n_{Cu^{2+}} \) was 16.2:1 at 3.0 V. With 0.5 mol l\(^{-1}\) sulfuric acid, the reacted molar ratio of \( n_{H^+}/n_{Cu^{2+}} \) were 886.9:1 at 3.0 V and 75.3:1 at 3.4 V, respectively. With 2.0 mol l\(^{-1}\) sulfuric acid, the \( n_{H^+}/n_{Cu^{2+}} \) was 486.8:1 at 3.4 V. Therefore, it was confirmed that the increasing sulfuric acid concentration improved the degree of the reaction during hydrogen ions participated in LECD process, resulting in the lower deposition rate of copper microcolumn under the same deposition voltage condition.

At the same time, it was found that the \( n_{H^+}/n_{Cu^{2+}} \) decreased with the increase of the voltage under each sulfuric acid deposition condition in table 1. Because of the increasing voltage, the electrode polarization and the electric field were enhanced, resulting in faster ions electromigration and ions reduction reactions per unit time. The reduced number of hydrogen ions and copper ions increased with increasing voltage, as was the case with 0.5 mol l\(^{-1}\) sulfuric acids in table 1. With 0.5 mol l\(^{-1}\) sulfuric acid, when the voltage value was increased by 0.2 V from 3.0 to 3.4 V, the reduction ratios of hydrogen ions were 1.37 (\( i_{H^+}/i_{H^+}^{3.0 V} \)) and 1.95 (\( i_{H^+}/i_{H^+}^{3.4 V} \)) times, respectively, but the reduction ratios of copper ions were 7.67 (\( i_{Cu^{2+}}/i_{Cu^{2+}}^{3.0 V} \)) and 23 (\( i_{Cu^{2+}}/i_{Cu^{2+}}^{3.4 V} \)) times, respectively. However, the copper ion reduction deposition rate was faster, resulting in the lower molar ratio of \( n_{H^+}/n_{Cu^{2+}} \), the same is true for other sulfuric acids.

In short, the \( n_{H^+}/n_{Cu^{2+}} \) molar ratio, which was influenced by sulfuric acid concentration, could intuitively reflect a competitive mechanism of the electrochemical reaction on the LECD, resulting in the inhibited deposition rate, the decreased diameter of copper microcolumn and the optimal surface morphology. The threshold voltage was also changed from 2.8 V to 3.4 V. However, the copper microcolumn diameter was limited by the anode diameter. Thus, the copper column diameter can be reduced by up to 50% by the effect of sulfuric acid.

| voltage(V) | \( i/(10^{-3} \text{A}) \) | \( \mu \text{m s}^{-1} \) | \( i_{H^+}/(10^{-6} \text{A}) \) | \( i_{Cu^{2+}}/(10^{-6} \text{A}) \) | \( n_{H^+}/n_{Cu^{2+}} \) |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2.8       | 0.013           | 0.043           | 94.66           | 5.34            | 35.5:1          |
| 2.9       | 0.125           | 0.305           | 112.07          | 12.93           | 17.3:1          |
| 3         | 0.16            | 1.61            | 142.4           | 17.6            | 16.2:1          |

Table 1. The \( n_{H^+}/n_{Cu^{2+}} \) molar ratio under different conditions.
4. Conclusions

Copper microcolumns were deposited by LECD under different sulfuric acid concentrations. Comparison of the deposition rates, deposition voltages, surface quality, and diameters of the obtained copper microcolumns allowed the following conclusions to be drawn.

1. During LECD, the deposition voltage can increase the deposition rate of the copper microcolumn to result in the bump and branch. However, the sulfuric acid concentration can decrease the deposition rate of copper microcolumn and inhibit the formation of bump and branch on the surface.

2. The lowest voltages at which deposition was observed produced copper columns with diameters of 76.5 μm (0.05 mol l$^{-1}$ sulfuric acid at 2.8 V), 14.6 μm (0.5 mol l$^{-1}$ sulfuric acid at 3.0 V), and 14.5 μm (2.0 mol l$^{-1}$ sulfuric acid at 3.4 V). The diameters obtained in the presence of the 0.5 and 2.0 mol l$^{-1}$ sulfuric acid concentrations were smaller than the anode diameter as increasing the voltage.

3. At each sulfuric acid concentration, the optimal surface morphology was obtained for the copper column deposited at a deposition rate of approximately 0.3 μm s$^{-1}$.

4. The competition reduction mechanism of hydrogen ion and copper ion was influenced by the sulfuric acid concentration on the LECD, leading to the low deposition rate, the high threshold voltage, the small diameter and the smooth surface morphology of copper microcolumn.

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