Effect of Polyethylene Glycol and Chloride Ions on Local Electrochemical Deposition of Micro Copper Columns

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Abstract. Local electrochemical deposition (LECD) is a very promising three-dimensional (3D) metal microstructure fabrication method. To fabricate smaller and better micro structures, a 20 μm micro anode and suppressor were used to reduce the diameter of a micro copper column and improve its surface morphology. Micro copper columns were deposited with a copper sulfate electrolyte, with or without polyethylene glycol (PEG) and chloride (Cl−) ions. The morphology and size of all deposited columns were analyzed at the same voltage, and the deposition mechanisms with PEG and Cl− were discussed. Results indicated that the 20 μm micro anode formed a micro copper column of diameter 30-40 μm, and the use of PEG and Cl− further decreased the diameter to 28.1 μm.

1. Introduction
Local electrochemical deposition (LECD) is a very promising three-dimensional (3D) metal microstructure fabrication method [1], as it only required simple and inexpensive equipment, a general environment, simple procedures, and widely available chemical materials. Ever since LECD was proposed by Madden in 1995 [2], it has been used to machine microstructures in the lab. Currently, microstructures fabricated by LECD include high-aspect-ratio copper columns, spring, nickel columns, and copper walls [2-5].

These studies have promoted the development of LECD. As the size of the anode is directly related to the deposited diameter of the micro column, different anodes (diameters ranging from 20 μm to 200 μm) were used [6-8]. Movement control methods for the anode were also studied to improve the deposited surface morphology, including shape of the bump and the deposited root [7, 9]. Additionally, the initial deposition gap has proven a key factor influencing the deposited threshold voltage and morphology of the microstructure [3, 10]. In order to fabricate different microstructures by LECD, complex programs designed by computer software were used to control the 3D movement of the anode and manufacture microstructures of different shapes [2, 4, 8, 11]. A hollow copper cylinder deposited by rotating the anode and the copper wall are the most typical examples of all microstructure shapes [5, 8].

In addition to these physical parameters and models, the deposition morphology is also affected by the additives. Additives are crucial to further improve the morphology and reduce the size. According to previous work, additives can cause grain refinement, inhibit or accelerate deposition, and burnish surfaces [5, 12-15]. In particular, after combining different additive species in a base solution, the effect of inhibition or acceleration is more distinct. For example, with bis-(3-sulfopropyl) disulfide, which is an accelerator used in electrochemistry, the deposition rate is higher, as it acts synergistically.
with chloride (Cl\(^-\)) ions [16]. However, Polyethylene glycol (PEG), which is a suppression additive, is used in the electrochemical deposition of copper [17, 18]. Although Cl\(^-\) shows an inhibition effect, the interaction of PEG and Cl\(^-\) can enhance the inhibition effect [19-22]. However, the effect of PEG and/or Cl\(^-\) on LECD has not been studied yet. Theoretically, the suppressor can lower the deposition rate of copper and may reduce the diameter of the micro copper column.

In this study, the effect of PEG and/or Cl\(^-\) on the deposition of a micro copper column via LECD was analyzed. The micro copper columns were deposited in three forms – without the additive, with only PEG as the suppressor (molecular weight = 10000), and with a combination of PEG and Cl\(^-\). The morphology and size of all deposited columns were analyzed at the same voltage, and the deposition mechanism with PEG and Cl\(^-\) was discussed.

2. Experimental

![Figure 1. Schematic of the experimental set-up for LECD](image)

Figure 1 shows the experimental setup. The anode used in this study was a 20 μm diameter platinum wire sealed in a glass tube (inner diameter = 100 μm), and the gap between the tube and wire was filled by an epoxy resin adhesive. One end of the Pt wire was welded with the conducting wire and connected to a DC power supplier, whereas the other end was ground by sandpaper, and polished with 0.5 μm Al\(_2\)O\(_3\) with a grinding machine, to expose the anode to the electroplating solution. Subsequently, the anode was installed in a 3D motion platform. The circuit contains the anode as well as the cathode. The cathode was a copper plate deposited with silver on a surface of dimensions 5 mm × 5 mm × 0.2 mm. It was then affixed to a metal substrate by a conductive adhesive. The substrate cured by the epoxy was placed at the bottom of the container. Finally, the cathode was connected to the ground of the DC power supplier by a conducting wire.

The experiment was conducted in two steps. In the first step, the anode was in contact with the cathode. After switching on the power, the anode was moved toward the cathode with a high resolution of 1 μm per step, until the current exceeded the threshold (100 mA), at which value the anode and cathode were in contact. The power was then turned off. The second step was the deposition of the column. The initial gap and deposition voltage were set by a software, such that the anode would ascend a certain distance (for example, 1 μm) toward the cathode. After setting the initial parameters, the electrolyte was poured into the container and the power was turned on again to commence electroplating.

LECD was carried out as follows: copper ions were reduced and deposited on the cathode and grew toward the anode under the action of electric field. When the growing column almost approached the anode, a sudden rise in current was detected, which exceeded the threshold and triggered the next step. The power was turned off immediately and electroplating was paused. After the anode ascended a certain distance to maintain the predefined gap, the power was turned on and electroplating continued.
again. This cycle was repeated until the copper columns reached an expected height. In this study, all Cu columns had the same height of 1000 μm.

3. Results and Discussion

3.1. Copper Column Deposited with Only Copper Sulfate Solution

Figure 2 shows the SEM morphologies of the copper micro columns deposited at different voltages (2.7 V, 2.8 V, 3.0 V, 3.2 V, and 3.3 V) without any additive. The concentration of CuSO₄·5H₂O was 200 g/L.

At 2.7 V, the copper column does not possess branches, as shown in Figure 2a; however, the surface is covered with some small particles, and the top shows cracks. On increasing the voltage to 2.8 V, the surface morphology does not exhibit particles or branches, and the top is flatter than at 2.7 V; meanwhile, the diameter decreases from 40.8 μm to 30.1 μm, as shown in Figure 2b. On further increasing the voltage to 3.0 V, branches and bumps appear on the trunk and top, respectively, as shown in Figure 2c. With increasing voltage to 3.2 V and 3.3 V, the branches and bump structure became increasingly pronounced, and the shape is no longer a pillar, as shown in Figures 2d and 2e.

Figure 2 indicates that the voltage has a significant effect on the deposition of the column, and a voltage of 2.8 V is optimum, as it provides better surface morphology and smaller diameter.

![Figure 2. SEM images of the copper columns deposited at different voltages. (a) 2.7 V, (b) 2.8 V, (c) 3.0 V, (d) 3.2 V, and (e) 3.3 V with only copper sulfate solution](image)
3.2. Copper Column Deposited with PEG Additive

Figure 3. SEM images of copper columns deposited at different voltages, with only PEG added to the sulfate electroplating solution (a) 2.7 V , (b) 2.8 V , (c) 3.0 V , (d) 3.2 V , and (e) 3.3 V

Figure 3 shows the effect of deposition voltage on the morphology of the copper column deposited in the sulfate solution with the PEG additive. PEG is a common suppressor and can block the copper surface and inhibit deposition [18]. In the experiment, the concentrations of CuSO\(_4\)·5H\(_2\)O and PEG were 200 g/L and 6 mg/L, respectively. Figure 3a shows that the column deposited at a low voltage (2.7 V) has a larger size, with a diameter of 36.3 μm; further, the surface is rough and without branches. However, the surface morphology appears better at the 2.8 V condition, for which the diameter decreases to 29.6 μm (Figure 3b). When the voltage is increased to 3.0 V, branches and bump structures appear (Figure 3c). With a further increase in voltage to 3.2-3.3 V, the columns transform into vines with many small branches, as shown in Figures 3d and 3e.

Based on Figure 3, the morphology at 2.8 V was deduced to be the best in different deposition voltages, with only PEG as the additive. Hence, the higher the voltage, the poorer the morphology.

3.3. Copper Column Deposited with PEG Additive and Cl\(^-\)

Comparing Figures 2 and 3, the PEG additive alone does not appear to cause improvement in the deposition quality of the copper columns, as the suppression effect of PEG requires Cl\(^-\) [21]. Therefore, PEG and Cl\(^-\) were added simultaneously, at concentrations of 6 mg/L and 0.5mg/L, respectively. The concentration of CuSO\(_4\)·5H\(_2\)O was 200 g/L. Figure 4 shows the morphologies of the copper micro columns deposited in the copper sulfate solution containing the PEG additive and Cl\(^-\) ions.
Figure 4. SEM images of copper columns deposited at different voltages, with PEG and Cl$^-$ in the sulfate electroplating solution. (a) 2.7 V, (b) 2.8 V, (c) 3.0 V, (d) 3.2 V, and (e) 3.3 V

Figure 4a and 4b show the columns deposited at 2.7 V and 2.8 V. PEG and Cl$^-$ together significantly improve the surface morphology, which does not exhibit grains, bumps, or branches in the middle or top of the column, and decrease the diameter to 30.5 μm and 28.1 μm, respectively. However, the column fabricated at 3.0 V shows many bumps, which make the surface rougher, as shown in Figure 4c. With increasing deposition voltage, the columns transform into vines with many small branches, as shown in Figure 4d and 4e.

Therefore, the combined addition of PEG and Cl$^-$ can dramatically improve the surface morphology and decrease the diameter of the columns at deposition voltages of 2.7 V and 2.8 V. The suppression effect of PEG and Cl$^-$ can decrease the grain size [17], thereby enhancing the smoothness and decreasing the diameter of the column.

3.4. Mechanism of Suppression Effect on Deposition of Copper Column

Copper ions driven by electric field are reduced to copper and grow into copper column at the cathode. Thus, the distribution of electric field on the surface of the copper column is not uniform as shown in figure 1. No uniformity lead to some problems of the surface grain size and cross-sectional diameter. Therefore, we hope to use PEG additive and Cl$^-$ to obtain good surface morphology.

The schematic diagram of mechanism of PEG is shown in figure 5a. It was adsorbed on the surface of the column with potential-dependence, thereby impeding the deposition of copper ions on the surface, and eventually resulting in a column with a smaller diameter than that without the PEG additive. However, the electric field become weak with copper column grown to make the absorption of PEG weak to desorb from the surface. In the meantime, owing to the chain molecular structure of PEG, PEG molecules are not very close together in the weak electric field region. Based on some reasons, there are some gaps between PEG molecules or PEG and copper column. And the gaps lead to weaker suppression effect than elsewhere. Consequently, these gaps enable the rapid deposition of copper ions driven by the electric field, resulting in a rougher surface. Therefore, the morphology in this case is poorer compared with the others. Although these gaps cause the surface to be uneven and
unsmooth, the average diameter decreases by 4.5 μm, compared with the diameter without using the additive at 2.7 V. With increasing voltage, the change in the diameter of the micro column becomes smaller.

Figure 5. Illustration of the suppression effect of the PEG additive and Cl$^-$ ions on column deposition: (a) with only PEG and (b) with PEG and Cl$^-$

However, Cl$^-$ ions can overcome this disadvantage. The mechanism diagram is shown in figure 5b. PEG interacts synergistically with Cl$^-$ and Cu$^{2+}$ / Cu$^+$ to inhibit the metal deposition [21, 22]. On the surface of the copper column, PEG and Cu$^{2+}$ / Cu$^+$ and Cl$^-$ combine to absorb the surface of copper column to form the clathrate that impede copper ions deposition. Cl$^-$ absorbed is closest to the copper column. At the same time, Cl$^-$ and Cu$^+$ can impede the deposition at these gaps region. Under the action of PEG and chloride ions, copper ions are firstly reduced to cuprous ions and then to copper on the surface of copper column. At the same voltage, the deposition rate is lower than that without Cl$^-$ ions. The suppression effect of PEG-Cu$^{2+}$/Cu$^+$-Cl$^-$ can lead to smaller-diameter columns and the more suitable the surface morphology. Because of the absorbed effect, the diameter is also reduced by about 10 μm at 2.7 V and 2 μm at 2.8 V, compared to that without the additive. The mechanism explains that PEG and Cl$^-$ not only improve the quality of the morphology, but also reduce the cross-sectional diameter in the experiment. Of course, some unknown mechanisms of PEG need to be explored further.

4. Conclusions
The effect of adding PEG and Cl$^-$ ions on LECD was studied. Micro copper columns were deposited with a micro anode of diameter 20 μm in three forms: (1) with PEG, (2) without PEG, and (3) with both PEG and Cl$^-$. The morphology and diameter of the micro copper columns were compared. Some conclusions can be drawn, as follows:

1) The 20 μm micro anode formed a micro copper column of diameter 30-40 μm. The voltage had a significant effect on the deposition of the column, and 2.8 V was the optimum voltage.
2) The addition of PEG slightly decreased the diameter, but resulted in poor morphology due to gaps between the adsorbed PEG molecules.
3) The interaction of PEG and Cl$^-$ decreased the diameter of the micro copper column 28.1 μm and avoided poor morphology.
5. Acknowledgments
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6. References
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