A Compatible and Efficient Fabrication of Bi-Continuous Nanoporous Copper Films

Sizhen Chen¹,², Chao Ren¹,², Penglei Zhang¹,², Yunna Sun¹ and Guifu Ding¹,*

¹ National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Shanghai Jiao Tong University, Shanghai, 200240, China
² School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China
Email: gfding@sjtu.edu.cn

Abstract. To cater to the application in various micro/nano devices, this paper reports a compatible and efficient approach combining electrodeposition and dealloying to fabricate bi-continuous nanoporous copper films. In the electrodeposition step, effect of concentration ratio of different ions, pH of the solution and cathode current density on the elementary composition and microscopic morphology of the deposited alloy are systematically investigated, obtaining an optimum condition with good stability and process compatibility. A uniform copper-zinc alloy with its zinc content improved to ~67 at.% is prepared under this condition. A uniform nanoporous copper with an average pore size of 150 nm is fabricated by ultrasonic assisted dealloying whose efficiency is significantly improved compared to free dealloying. This method is promising to be used in the mass production of nanoporous copper films, benefiting researches on various practical applications in micro/nano devices.

1. Introduction

Due to their high surface-to-volume ratio, low density and good electric and thermal conductivity, metallic nanoporous materials have attracted considerable attention in various fields, such as catalysis, sensors and actuators, fuel cells etc. [1-5]. As a typical metal nanoporous material, nanoporous copper (NPC) has become more popular than other precious metals, because of the advantages of abundant sources, low cost, and diverse preparation methods. 

Till now, many physical and chemical methods have been proposed to fabricate nanoporous copper materials. Compared with the template and casting methods [6-7], preparation of nanoporous copper by the dealloying process has been widely studied because of its flexibility and low cost. The principle of the dealloying method is to selectively dissolve the less noble component from the alloy through chemical/electrochemical methods while the residual component rearranges to form a nanoporous structure by choosing suitable alloy precursors and controlling the dealloying conditions. Chen et al. [8] fabricated NPC with pore sizes ranging from ~15 nm to ~200 nm by selective corrosion of the melting single-phase Cu30Mn70 alloy in HCl solutions with different duration. A hierarchically structured micro/nanoporous copper [4] was formed in a 3 wt.% HCl solution at 50 °C with a multi-phase Cu-Al alloy synthesized by a pack cementation method as its precursor. In the study by Yang et al. [9], an enhanced bulk nanoporous copper with a three-dimensional bi-continuous porous structure was obtained by dealloying of Cu30Zn70 precursors which were synthesized through a casting process at 900 °C. It has been found that free corrosion in acid solution is a common method for dealloying. However, the hydrogen bubbles generated by the dissolution of Zn may remain in the nanopores formed by the early
dealloying period, which would hinder the contact between the corrosive liquid and the undealloyed layer, delaying the further dealloying process. Besides, prior to dealloying, the preparation of the precursor alloys greatly affects the application of the nanoporous structures. Conventional methods such as casting and melting require a high working temperature and the prepared alloys are mostly bulk materials, which damages the process compatibility and limits the application of NPC in micro/nano devices. Meanwhile, manufacturing costs will be increased if we choose the sputtering process [10]. A compatible co-electrodeposition process [11-12] has been proposed to prepare a Cu-Zn alloy precursor, whose thickness can be tuned by controlling the deposition time. Whereas, to meet the component threshold of the less noble element (Zn), the concentration of Cu$^{2+}$ and Zn$^{2+}$ ions in the electrolyte solution differ largely. Given the consumed ions cannot be replenished from a suitable alloy anode, the bath system of the co-electrodeposition is erratic.

In this study, we propose a compatible and efficient two-step fabrication of bi-continuous nanoporous copper films, combining electrodeposition and dealloying. In the electrodeposition step, the Cu-Zn alloy precursors are obtained by co-electrodeposition at a constant current density. In addition, the effects of concentration ratio of different ions, pH and cathode current density on the composition and morphology of the deposited alloy layer are investigated systematically. In the dealloying step, the dealloying time is controlled in different concentrations of hydrochloric acid to obtain uniform and stable nanoporous copper, and the dealloying efficiency is significantly improved through the assistance of ultrasound during the process.

2. Methods

As is shown in figure 1, nanoporous copper films were fabricated by the electrodeposition of Cu-Zn alloys and a subsequent dealloying process.

![Figure 1](image)

**Figure 1.** Schematic of the proposed compatible and efficient method to fabricate nanoporous Cu by electrodeposition of Cu-Zn alloys and a dealloying process.

2.1. Substrate Preparation

Polished monocrystalline silicon wafers coated with thin layers of titanium (Ti) and copper (Cu) by magnetron sputtering were prepared as the substrate to provide a super smooth surface for
electrodeposition. It should be noted that the titanium film served as an adhesion layer and the copper film acted as a conductive layer respectively. After being coated with Ti/Cu, the wafer was cut into square pieces of 1.5×1.5 cm² by laser for use. Before electrodeposition, the substrate was immersed into 7 wt.% H₂SO₄ to remove the oxide layer on the surface and rinsed with deionized water.

2.2. Co-electrodeposition of Cu-Zn Alloy Precursors

The electrodeposition was performed at a constant current density in a two electrodes system, where a titanium mesh coated with platinum was chosen as the anode and the prepared substrate as the cathode. The working current was provided by an adjustable DC power supply (GPD-3303S, GWINSREK). The electrolyte solution for electrodeposition was composed of CuSO₄·5H₂O, ZnSO₄·7H₂O, with Na₃C₆H₅O₇·2H₂O as the complex agent. Concentration ratio of Cu²⁺ and Zn²⁺, pH and cathode current density were studied to obtain an optimal condition for the co-electrodeposition of Cu-Zn alloy. Three kinds of baths with different concentration of CuSO₄ are listed in table 1. pH of the electrolyte solution was adjusted by the addition of H₂SO₄ and NaOH. Because temperature also has an important effect on electrodeposition, it was set at 25 °C in all deposition process. After deposition, the prepared Cu-Zn alloy precursors were rinsed with deionized water and dried at 65 °C for the following dealloying.

| Table 1. Chemical composition of electrolyte. |
|---------------------------------------------|
| Bath | CuSO₄ (M) | ZnSO₄ (M) | Na₃C₆H₅O₇ (M) |
|-------|-----------|-----------|---------------|
| Bath1  | 0.02      | 0.3       | 0.5           |
| Bath2  | 0.03      | 0.3       | 0.5           |
| Bath3  | 0.06      | 0.3       | 0.5           |

2.3. Formation of Nanoporous Copper

Cu-Zn alloy precursors were dealloyed in HCl solutions with various concentrations (0.025M, 0.05M, 0.1M) to fabricate nanoporous copper films. The process temperature was set at 25 °C. Besides, to promote the dealloying process, the selective dissolution of Zn was performed in an ultrasonic cleaner (TES-1010, TIME) to help hydrogen bubbles get rid of the pores. The dealloyed specimens with nanoporous structure were then rinsed with deionized water and dried at 65 °C.

2.4. Characterization

The morphology and chemical composition of electrodeposited Cu-Zn alloy precursors and dealloyed nanoporous copper were characterized by a field emission scanning electron microscope (FESEM) (Ultra55, ZEISS) combined with an EDS analyzer.

3. Results and Discussion

3.1. Preparation of Cu-Zn Alloy Precursors by Electrodeposition

To obtain uniform bi-continuous nanoporous copper by dealloying, the alloy precursor should meet two requirements [13]; (1) There should be a large difference in the standard metal/metal-ion electrode potentials between copper and another less noble (LN) element (at least a few hundred millivolts). (2) The composition of the less noble element should surpass the component threshold. Therefore, Cu-Zn alloy is an excellent precursor for dealloying with the difference in standard electrode potential between Cu and Zn as 1.1 V. It was reported that [14] Cu-Zn alloys with Zn content of ~70 at.% are more likely to obtain bi-continuous nanoporous copper with open pores through dealloying.

In this study, Cu-Zn alloys were fabricated by electrodeposition, which is a process of depositing a thin layer of metal, alloy or composite material on the surface of a conductive solid by electrochemical methods. Based on electrodeposition theory, that the precipitation potential of the two metals are very close is necessary for co-electrodeposition, which can be adjusted by the addition of a complex agent to regulate the activity of metal ions. To obtain better process compatibility, trisodium citrate (C₆H₅Na₃O₇)
was chosen as the complexing agent, whose complexing ratio to Cu²⁺ and Zn²⁺ change with pH. For a co-electrodeposition system, several factors impact the preparation of the alloy. Herein, the effects of concentration ratio of Cu²⁺ and Zn²⁺, pH of the solution and cathode current density on the composition and morphology of the alloy have been investigated step by step.

Electrolyte solutions with the concentration ratio of Cu²⁺ and Zn²⁺ as 1:15 (Bath1), 1:10 (Bath2) and 1:5 (Bath3) were prepared. Based on different baths, pH and cathode current density were regulated to obtain a uniform and stable Cu-Zn alloy with the composition of Zn at ~70 at. %.

3.1.1. The Effect of pH on Deposited Alloys. In Bath1, pH is firstly investigated. The raw electrolyte solution with 0.02M CuSO₄·5H₂O, 0.3M ZnSO₄·7H₂O and 0.5M Na₃C₆H₅O₇·2H₂O has the pH of 5.25. Cu-Zn alloys prepared in this solution have a brassy appearance (figure 2a) with microscopically unevenly spherical grains (figure 2g). EDS analysis manifests that the Zn content in this alloy is only 23.74 at.%. Figure 2b-c show that alloys obtained under pH of 6 and 6.5 are heterogeneous with a distinct color division on the surface, which indicates the instability of the electrolyte solution. When pH is regulated to 7, the deposited Cu-Zn alloy shows a uniform light gray surface macroscopically (Figure 2d) with a regular grain size (Figure 2h) and the Zn content is measured at 67 at.%, which is close to ideal. When the pH rises to 7.5, as is shown in Figure 2e, the alloy surface has brassy and green divisions. Continue to increase the pH, as is shown in Figure 2f, the alloy coating begins to show a uniform green color and large protruding grains can be observed on SEM images of the microscopic morphology. Besides, the Zn content of the alloy has been reduced to ~30 at.%. The complexing ability of citrate ion to Cu²⁺ is stronger than that to Zn²⁺. When the pH is 7, the difference in complex ability reaches the maximum value, which significantly reduces the activity of Cu²⁺ in solution, favoring the deposition of Zn. The above experiments demonstrate that in Bath1, it is most likely to obtain a uniform Cu-Zn alloy with its Zn content of ~70 at.% when pH = 7.

![Figure 2](image_url)

3.1.2. The Effect of Cathode Current Density on Deposited Alloys. With the pH of deposition solutions fixed at 7, the alloy coatings obtained under different cathode current density (J) are shown in figure 3. It is depicted in figure 3a-b that, Cu-Zn alloys deposited under the current density of 3 mA/cm² and 4 mA/cm² have macroscopically smooth and uniform surfaces and the regular grains can be observed by the SEM images in figure 3f-g. When J is larger than 5 mA/cm², the distribution of current density on the substrate is uneven, and the edge appears black due to the concentration of current density (figure 3c-d). EDS analysis shows that the Zn content in the edge area is much higher than the central area. When J is 6 mA/cm², the Zn content even reaches 100%. For the central area, as shown in figure 3e, the Zn
content in Cu-Zn alloys increases from 60% to 82% with the increase of current density. For a given cathode current density, the deposition rate of the more noble metal (Cu) is relatively closer to the critical current density. Therefore, increase of cathode current density is more likely to improve the deposition rate of the less noble metal (Zn), thereby increasing the content of Zn in the alloy. Besides, as J increases from 3 mA/cm$^2$ to 6 mA/cm$^2$, the microscopic morphology of the alloys (figure 3f-i) changes from regular square grains to sharp cone-shaped grains with fuzzy boundaries. Overall, although the increase of cathode current density is beneficial to obtain a higher Zn content, the uneven distribution of the current density will make the coating lose its uniformity, which makes it difficult to obtain uniform nanoporous copper by subsequent dealloying process. Therefore, the optimal condition in Bath1 is pH=7 and J=4 mA/cm$^2$ (condition1), in which the prepared Cu-Zn alloy shows a uniform appearance of light gray with regular and compact grains microscopically, and the Zn content is ~67 at.%.

![Figure 3. Appearance of Cu-Zn alloys obtained in Bath1 at the current density of (a) 3 mA/cm$^2$, (b) 4 mA/cm$^2$, (c) 5 mA/cm$^2$, (d) 6 mA/cm$^2$. (e) Change of the atom percentage of Cu and Zn alloys with the current density. SEM of the micro morphology of Cu-Zn alloys obtained in Bath1 at the current density of (f) 3 mA/cm$^2$, (g) 4 mA/cm$^2$, (h) 5 mA/cm$^2$, (i) 6 mA/cm$^2$.](image)

3.1.3. Optimization of Concentration Ratio of Cu$^{2+}$ and Zn$^{2+}$. The same method was applied to Bath2 and Bath3. The best condition in Bath2 is pH = 6, and J = 8 mA/cm$^2$ (condition 2) while that in Bath3 is pH = 6, and J = 15 mA/cm$^2$ (condition 3). As is shown in Figure 4, the surface of the alloy layer obtained under these two conditions has divisions in microscopic morphology, while the Zn content of the two structures is similar, being ~75 at.% under condition 2 and ~65 at.% under condition 3, respectively.
Figure 4. The appearance and morphology of Cu-Zn alloys obtained in (a)-(c) Bath2 with cathode current density of 8 mA/cm² and pH of 6 and (d)-(f) Bath3 with cathode current density of 15 mA/cm² and pH of 6.

Size of the substrate and volume of the electrolyte solution are changed to conduct further research on the above three conditions. Only the Cu-Zn alloy prepared under condition 1 can still maintain its uniformity and stability in elementary composition and microscopic morphology, as is shown in figure 5. Therefore, the optimal condition for the fabrication of Cu-Zn alloy precursor in this study is shown in table 2, with its Zn content at ~67 at.% and the thickness can be tuned by controlling the deposition time.

Table 2. The optimal condition of electrodeposition for fabrication Cu-Zn alloy precursor.

| CuSO₄ (M) | ZnSO₄ (M) | Na₃C₆H₅O₇ (M) | pH  | Current Density (mA/cm²) |
|-----------|-----------|----------------|-----|--------------------------|
| 0.02      | 0.3       | 0.5            | 7   | 4                        |

Figure 5. The SEM image and EDS mapping of the Cu-Zn alloy precursor obtained in Bath1 with the cathode current density of 4 mA/cm² and the pH of 7.

3.2. Fabrication of Nanoporous Copper by Dealloying

3.2.1. Free Dealloying. Hydrochloric acid is chosen as the electrolyte for dealloying to conduct the selective dissolution of Zn. The acid concentration has a critical effect on the evolution of the microstructure, which determines the uniformity and stability of the prepared nanoporous copper. As is
shown in Figure 6, the dealloying process in HCl with concentration of 0.025M, 0.05M, 0.1M are investigated. Figure 6a-c depict that, in the initial stage of dealloying in 0.025M HCl, some small pores were formed on the surface of the film. With the progress of dealloying, the porous structure did not deepen into the bulk while a locally smooth surface began to appear. After 48 hours of dealloying, no continuous nanoporous structure was formed. A low acid concentration results in a low atom mobility rate at the solid/electrolyte interface [15]. After Zn atoms in the first layer are selectively dissolved, the coordinated copper atoms remain as adatoms on the surface, leading to the enrichment of Cu atoms, which blocks the dealloying channel, and hinders the further reaction. Finally, the copper atoms on the surface migrate slowly and join together to form a stable and smooth surface. In 0.05M HCl, a uniform bi-continuous nanoporous copper with an average pore diameter of 120 nm (figure 6e) was gradually formed within 36 h. Extending the dealloying to 48 h, the pore size was slightly coarsened while the nanoporous structure still exists. When the concentration of HCl was increased to 0.1M, as shown in figure 6g-i, a continuous NPC can be obtained in 24 h. However, with the further extension of the dealloying time, the NPC became heterogeneous and the structure collapsed. This indicates that NPC is unstable in concentrated acid solutions which promotes the mobility of Cu atoms at the solid/electrolyte interface to form a compact structure of nanoparticles with lower surface energy.

The above experiments show that it is more difficult to form a bi-continuous NPC with open pores in HCl solution with low concentration. Although increase in acid concentration can improve the dealloying efficiency, the prepared NPC tends to evolve into nanoparticles with lower surface energy in concentrated solutions. Overall, in 0.05M HCl, a uniform bi-continuous NPC with a suitable pore size can be obtained by controlling the dealloying time.
3.2.2. Ultrasonic Assisted Dealloying. The hydrogen bubbles generated by the reaction of HCl and Zn may block the nanopores formed by dealloying, preventing the contact between electrolyte solution and the undealloyed alloy, which will delay the dealloying process. Therefore, to improve the efficiency of dealloying, ultrasonic assistance is applied to promote the escape of bubbles. As is shown in figure 7, in 0.05M HCl solution, with the aid of ultrasound, after 5 h of dealloying, a uniform and continuous NPC with an average pore diameter of 150 nm can be obtained. Compared with free dealloying, the efficiency is improved 7 times. Extending the dealloying time to 7 h, the nanoporous structure can still exist stably, which indicates its potential in the efficient fabrication of a stable and uniform NPC.

Figure 7. SEM images of NPC produced by dealloying Cu-Zn alloys with ultrasonic assisted 0.05M HCl for 2 h, 5 h, 7 h.

4. Conclusion
In summary, we have proposed a compatible and efficient two-step fabrication of bi-continuous nanoporous copper films by electrodeposition of Cu-Zn alloy and a dealloying process. Trisodium citrate is chosen as the complexing agent in the solution of electrodeposition for the difference in its complexing ability to Cu$^{2+}$ and Zn$^{2+}$. In this study, concentration ratio of Cu$^{2+}$ to Zn$^{2+}$, pH of the solution and cathode current density are regulated step by step to investigate their effect on the elementary composition and morphology of the deposited alloys. Compared to previous studies, we obtain a uniform Cu-Zn alloy with a higher atom percentage of Zn reaching 67 % at the same concentration ratio of Cu$^{2+}$ to Zn$^{2+}$ with pH = 7 and J = 4 mA/cm$^2$, which makes the process more flexible and compatible. 0.05M HCl is selected as the best concentration for dealloying, in which a stable and uniform bi-continuous NPC can be formed. Besides, ultrasonic assistance is applied to promote the escape of hydrogen bubbles generated during the dealloying process. Compared with free dealloying, the efficiency is improved 7 times. This compatible and efficient method with the characteristic of low cost is promising to be applied to the mass production of stable and uniform bi-continuous nanoporous copper films, which will promote researches on the application of NPC in catalysis, sensors, heat dissipation for micro/nano devices.

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