Abstract

Copper-tin (Cu-Sn) composite films were coated on Cu foil by electroplating. The electroplating bath contained 25 g/L SnCl₂, 4 g/L CuSO₄ and 180 g/L K₂P₂O₇. The composite film was deposited with 1 A/dm² current density at 25 °C. A new kind of porous Cu film was produced by dealloying this Cu-Sn composite film in 1 mol/L acetic acid solution with 0.5 A/dm² at 25 °C. The regularity in the porous Cu film morphology was optimized by changing electroplating and dealloying durations. Herein, the electroplating durations were chosen as 30 seconds, 1, 5 minutes and dealloying durations were selected as 1, 2, 10 minutes. The composition and the morphology of Cu-Sn composite films before and after the dealloying procedure were characterized by energy dispersive spectrometer (EDS) and scanning electron microscopy (SEM). EDS results showed that the Sn content in the Cu-Sn films after electrochemical dealloying process was reduced significantly, generating porous morphology in the remained Cu rich film. The morphological analyses revealed that the composition and the pore size distribution in the remained Cu rich film could be controlled by changing the electroplating and dealloying durations.

1. Introduction

Porous materials are increasingly being used as catalysis, sensor, actuators and electrodes for fuel cells because of their unique structural and morphological properties [1-4]. The tunable dimensions of their pores at atomic, molecular and nanometer scales improve their abilities to absorb and interact with atoms, ions, and molecules on their large interior surfaces. During the past few decades, porous materials have been usually fabricated by metal organic deposition [5] and template directed electrochemical techniques [6]. However, these processes are generally difficult to control and time consuming. In addition to them, sol-gel [7, 8], plasma hydrogenation [9] and pulsed laser ablation methods have been used to fabricate porous materials [10]. However, the fact that these methods are mostly difficult to handle, involve many steps and require long time they have not commercialized yet. On the other hand, it is unique recently that dealloying process is used to produce porous materials pioneered by the work in Refs. 11, 12 and 13.

During the latest decade, A.J. Forty et al. have suggested that dealloying process, which is a well-known etching technique, can be used to produce a wide range of porosities in the materials. A.J. Forty et al. first studied the morphology of the microstructures in detail after immersing the Ag-Au alloy in nitric acid [11]. Herein, dealloying refers to a selective dissolution of one or more components out of an alloy leaving a residual noble metal with porous structure [12]. Therefore, as in the galvanic corrosion, the more electropositive element remains in the film whereas the more electronegative element is corroded and dissolved in the electrolyte, leading a ‘sponge’ like morphology. Erlebacher et al, have discussed the mechanism of dealloying process [13]. They have proved that how the nano porosity evolves during the alloy dissolution, much attention has been devoted to the fabrication of porous materials by dealloying. During dealloying process, the resulting porous material is the product of interfacial phase separation of materials [14]. Starting from Ag-Au alloy, most of the report mention the porous metals formation as a result of the dealloying from single-phase solid solution systems. Other than that, A.J. Forty et al. and Erlebacher et al. have produced simple and homogeneous porous microstructure through Au-Ag-Pt, Cu-Pt, Cu-Au, Cu-Sn systems [15-18]. Therefore, a number of porous metals, including gold, silver, platinum, nickel and copper, have been synthesized using dealloying approach. The focus of this work is on synthesizing porous structure of copper by changing the electroplating and dealloying durations using dealloying technique from Cu-Sn alloy and studying the fundamental structural properties of the remaining porous film. SEM study is to examine surface morphology. EDS analysis is used to determine the amount of Sn in the film before and after dealloying process.

2. Experimental Procedure

![Figure 1. Process flow of fabrication of porous Cu Film](image-url)
Fig. 1 shows the schematic diagram of the process flow. Firstly, Cu film cleaned with ethanol and followed by activating in mixture of sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) and then cleaned in deionized water for 40 seconds each, respectively. After cleaning and activating part, Cu-Sn composite films were coated on Cu foil by electroplating. The electroplating bath contained 25 g/L SnCl₂, 4 g/L CuSO₄ and 180 g/L K₂P₂O₇. The composite film was deposited with 1 A/dm² current density at 25 °C. In electroplating, durations were chosen 30 seconds, 1 and 5 minutes. After plating, the sample was rinsed by deionized water to remove the residual plating solution, then composite films dried 12 hours in vacuum oven at 80°C. At last, the samples were immered 1 mol/L in acetic acid solution to fabricate porous Cu films. A new kind of porous Cu film was produced by dealloying this Cu-Sn composite film with 0.5 A/dm² at 25 °C. Morphologies and microstructures of the before and after the dealloying procedure were characterized by SEM and EDS. The detailed process parameters are listed in Table 1.

### Table 1. Process parameters for fabrication porous Cu films

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Electroplating time (min)</th>
<th>Dealloying time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

3. Results and Discussion

EDS results showed that the Sn content in the Cu-Sn films after electrochemical dealloying process was reduced significantly. The detailed before and after electrochemical dealloying A, B and C samples weight content of Cu and Sn are listed in Table 2.

### Table 2. EDS results of Sn-Cu alloys

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before Dealloying</th>
<th>After Dealloying</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu (wt %)</td>
<td>Sn (wt %)</td>
</tr>
<tr>
<td>A</td>
<td>56.26</td>
<td>43.74</td>
</tr>
<tr>
<td>B</td>
<td>34.25</td>
<td>65.75</td>
</tr>
<tr>
<td>C</td>
<td>16.45</td>
<td>83.55</td>
</tr>
</tbody>
</table>

For C sample, the agglomeration forms in the structure due to long electroplating time. After dealloying, Sn dendrites present and only large voids formed in C2 matrix. The excessive large voids are not as good as we expected because of constructing the non-continuous porous structure. On the other hand, the dendrite morphology known as “whisker” is not suitable for causing heterogeneous structure and loss of electrical conductivity due to short circuit.

Whisker growth is still phenomenon, but it is known that whisker formation is encouraged by fundamentally compressive stresses. These stresses is essentially caused by stresses induced by the diffusion of different metals and residual stresses originated by electroplating. In detail, the main reasons are irregular growth of copper-tin particles compound at ambient conditions [19]. In C sample, the non-uniform agglomerates form and diffusion between copper and tin particle can not properly proceed as a result of excessive long plating time. Therefore, overstress is generated in composite film. Correspondingly, irregular dissolution from these agglomerates occurs during dealloying process and then whiskers form.

**Figure 2.** SEM images of the Sn-Cu alloys before (1) and after (2) electrochemical dealloying
4. Conclusion

In this study, Cu-Sn composite films are produced in different electrochemical plating and dealloying conditions. The SEM results suggest that the porous structure can be fabricated by dealloying process. We obtained optimal porous morphology with 1 min plating and 2 min dealloying time among other composite films.

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References