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Bilayer nanoporous copper films with various morphology features synthesized by one-step dealloying

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ABSTRACT

The newly designed bilayer Cu-Al precursor films with different Cu contents were prepared by magnetron co-sputtering. Through dealloying the precursor films, bilayer nanoporous copper (NPC) films with various morphology features were synthesized. The impacts of the features of precursor films and dealloying solution species on the final NPC film products were investigated. The direct evidence of the process of how dealloying front penetrates into the interior of precursor films was revealed. Our findings not only help understand the mechanisms occurring during the dealloying process of copper-based films, but also bring inspirations of manufacturing other novel NPC materials in the future.

1. Introduction

Nanoporous metals (NPMs) with extremely large specific surface area and tunable porosity have been extensively studied due to their potential technological applications in catalysts [1–3], surface-enhanced Raman scattering substrates [4,5], energy storage [6,7], and microfluidic flow controller [8,9]. Among various synthesis approaches, dealloying either by chemical or electrochemical process has been widely demonstrated to be effective in producing a variety of NPMs (e.g., Au, Ag, Ni, Pt, Cu,etc.) [5,10–14]. In comparison with the nanoporous noble metals, nanoporous copper (NPC) has aroused even broader concerns because of its huge cost advantages in practical use.

The microstructure and composition of the alloy or metallic glass precursors for making NPC has been extensively studied as they certainly influence morphology features of the final as-dealloyed NPC [15,16]. Tuning the fabrication technique is desired as it largely determines the microstructure and composition of precursors. Up till now, powder metallurgic and melt-spun methods are the most common techniques adopted to synthesize the alloy or metallic glass precursors for the preparation of NPC [14–18]. As a powerful and popular method, however, magnetron sputtering technique to synthesize precursor films for the fabrication of NPC films has been barely reported. In the case of Cu-Al precursor thin films studied in this paper, relative researches are still lacking and no detailed studies on the impact of Cu-Al precursor film on the final NPC films have been reported.

As a novel functional material, one major challenge for NPMs including NPC is to be compatible with micro/nano fabrication technology and simple integration in micro-devices including solar cells and solid-state micro-batteries [19]. In comparison with powder metallurgic method, the control of precursor film thickness via magnetron sputtering is more convenient and the film size and thickness can be tailored to be extremely small [20]. Furthermore, the constituent distribution of precursors fabricated by metallurgic process can only be uniform and the design of a novel asymmetrical architecture seems impossible. However, method of magnetron co-sputtering provides more possibilities and broader room for the regulation and control of constituent distribution of precursors, e.g. bilayer or multilayer-like precursor films with various constituent ratio within each layer. Therefore, magnetron sputtering becomes an excellent choice for the achievement of this purpose.

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In this paper, magnetron co-sputtering method is applied to produce Cu-Al precursor films with different Cu contents. These as-deposited precursor films are whereafter dealloyed in acid and alkaline aqueous solution to produce NPC films with different morphology features. Impacts of the precursor film and dealloying solution species on the final NPC film products are investigated. On this basis, bilayer precursor films are deposited for the preparation of bilayer NPC films with different nanoporous structures within each layer to take full advantages of thin film technology. Besides, we obtain direct evidence of the process of how dealloying front penetrates into the interior of precursor films with time.

To sum up, our study highlights the importance of precursor design in the preparation for NPC films and provides the strategy for the first time to acquire bilayer NPC films via one-step dealloying.

2. Experiment

Cu target (99.99%) and Al target (99.99%) were co-sputtered onto Si (100) substrate to produce the Cu-Al alloy precursor films by magnetron sputtering. The chamber was evacuated to a base pressure of 1×10^{-4} Pa prior to deposition. To ensure a homogeneous deposition over a large surface, the optimal co-deposition parameters were determined to be rotated at a speed of 20 RPM at argon partial pressure of 1.8 Pa without deliberate heating during sputtering.

The composition of the films was controlled by varying the deposition rates to produce the alloy precursor films with a nominal atom ratio of $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ with a fixed thickness of about 1 μm. Specifically, the deposition rate of single Al target was measured to be 0.3 nm/s and those of single Cu target were 0.1 and 0.2 nm/s for the case of $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ films, respectively. The precise composition ratio of the precursor films was confirmed consistent with our design by performing Rutherford scattering spectrometry (RBS) measurement with 2.8 MeV He ions on films deposited on a carbon substrate under identical deposition conditions. Besides, two series of bilayer precursor films simultaneously consisting of $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ were prepared by successive deposition at various deposition rates with different order.

Chemical dealloying of all Cu-Al alloy precursor films was performed in 0.5 M NaOH and 2 M H_2SO_4 aqueous solutions at room temperature for different dealloying time to prepare NPC films. The dealloying experiments were carried out in Petri dishes sealed by parafilm to isolate from the air for the purpose of avoiding oxidation. When achieving the desired etching time, the samples were rinsed in deionized water and dehydrated alcohol for several times and then dried in nitrogen gas flow to remove the residue chemical substances and avoid potential oxidation.

Phases of precursor films were identified by X-ray diffraction (XRD) using a Cu Kα radiation. Microstructures of the as-deposited and as-dealloyed films were characterized by plan-view and cross-section scanning electron microscopy (SEM) at the same time. SEM observations were performed on FEI NanoSEM 430 microscope operating at 10 kV. For cross-section SEM observations on the interior part of as-dealloyed NPC films, the samples were cleaved using a diamond tip. The chemical composition of the films was determined by energy dispersive X-ray spectroscopy (EDS) performed on the cross-section samples.

3. Results and discussion

3.1. Influence of precursor films on the microstructures of NPC

Two types of Cu-Al alloy films with a nominal composition of $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ were prepared by magnetron co-sputtering to act as precursors for the subsequent fabrication of NPC films by chemical dealloying. The effect of phase composition and grain structure of precursors on nanoporous morphology of the as-dealloyed NPC films were studied in this research. Fig. 1 shows XRD patterns of the as-deposited $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ precursor films. The peak position was calibrated through the comparison with the Si (100) peak whose position is 69.133° and the 2 theta range of 25–67° is intercepted out as the peak of Si (100) substrates is too strong. XRD results illustrate both AlCu and $CuAl_2$ phases are observed in both precursor films, while Al phase only exists in the $Cu_{25}Al_{75}$ films. With the decrease of Al contents, Al phase disappears and AlCu phase becomes to play a more dominant role in the precursor films.

Fig. 2 (a, b) and (c, d) show SEM images of film surface and internal cross-section of the as-deposited $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ precursor films, respectively. It indicates that the as-deposited $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ films consist of irregular-shaped through-thickness columnar grains. The statistical in-plane grain size for $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ films is 75 ± 17 nm and 87 ± 21 nm, respectively. The high aspect-ratio of the through-thickness columnar grains results from the anisotropy growth velocity in the process of co-sputtering, in which the mixture of Cu and Al atoms will hinder the mobility of both atoms and thus lead to a limited coalescence and coarsening effect at the surface [21]. Besides, most columnar grains are closely arranged together and no distinct gaps are observed between columnar grains. Whereas the edge profile of columnar grains in $Cu_{25}Al_{75}$ films is more smooth compared with that in $Cu_{40}Al_{60}$ films.

Plan-view and corresponding cross-section SEM images of the NPC films dealloyed from $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ precursor films are illustrated in Fig. 3(a and b) and (c, d). Both the NPC films are fabricated through chemical dealloying in 0.5 M NaOH aqueous solution for 200 min at room temperature. The EDX analysis (insets in Fig. 3(b, d)) indicates most Al element is leached out from the precursor films. It should be noted that in both cases, there still remains a slight residual Al in NPC films because of the low solubility of AlO_2^- [16]. An extended dealloying time will not lead to a decrease in proportion of Al element but cause the formation of Cu_2O nanoparticles as reported in Ref. [4] instead of nanoporous structures, which shows the completion of dealloying process. However, the nanoporous structures of these two kinds of NPC

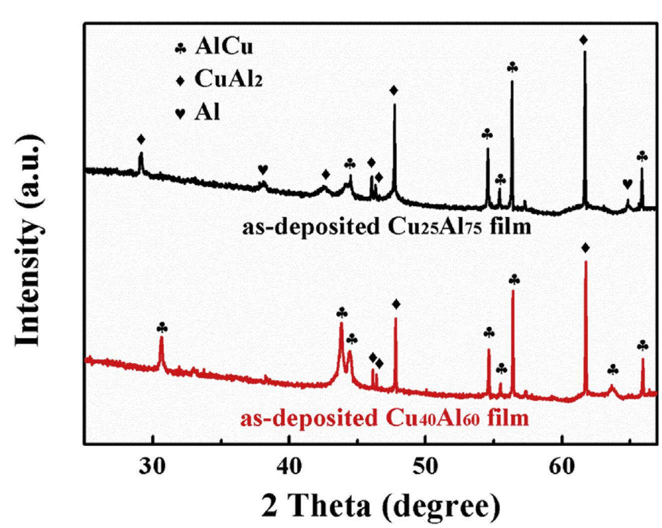

Fig. 1. XRD patterns of the as-deposited $Cu_{25}Al_{75}$ and $Cu_{40}Al_{60}$ films. The XRD patterns are identified by the database: Al (PDF#04-7807), AlCu (PDF#26-0016) and $CuAl_2$ (PDF#25-0012).