



Formation of three-dimensional nano-porous silver films and application toward electrochemical detection of hydrogen peroxide



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ABSTRACT

By using the chemically dealloying method, three-dimensional nano-porous silver films (3-D NPSFs) are fabricated into a novel sensor for detecting hydrogen peroxide. The precursor films are prepared by high vacuum magnetron co-sputtering. High-resolution transmission electron microscope (HRTEM) and scanning electron microscope (SEM) are taken to investigate the structure and the micro morphology of the precursor films and nano-porous films. We find that the precursor films are composed of glassy matrix and nanocrystallines. After dealloying, the films exhibit a combination of homogeneously distributed pores and silver filaments, and exhibit an open, three dimensional bicontinuous interpenetrating ligament-channel structure. Thickness and morphology of the films can be easily controlled by the sputtering time and alloy composition of the precursor films, respectively. In addition, NPSFs show a good linear responding for the concentration of hydrogen peroxide in phosphate buffered solutions, which indicates NPSFs could be a promising electrochemical material for hydrogen peroxide detection.

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1. Introduction

Different from bulk materials, thin film materials own unique physical and chemical properties [1,2]. The development of the thin film technology has brought great changes to human life. For instance, the discovery of giant magnetoresistance effect has a great impact on the storage of information [3,4]. In addition, nano-porous materials have attracted the attentions of many scientists and engineers. Due to the special microstructure, nano-porous metals exhibit large specific surface area and reveal lots of peculiar physical, chemical and mechanical properties. Among all metals, nano-porous silver has been extensively exploited in a variety of applications that range from catalysis, through antibacterial activity, to surface enhanced Raman scattering, [5–7] etc. Various methods, such as template-based, heat treatment of electrospun nanofibers, electrochemical and dealloying are currently used to obtain the porous silver nanostructure [8–10]. However, most studies focus on nano-porous silver particles or hollow spheres. There are few reports referring to the fabrication of nano-porous silver films (NPSFs). In our views, due to the three-dimensional porous structure, NPSFs are expected to have high electrical conductivity and more active sites per unit area for chemical reaction process.

As a well-known oxidizing agent, hydrogen peroxide is employed in various fields, such as cleaning products, disinfection and wastewater treatment [11–13]. Thus, it is important to measure the hydrogen peroxide concentration. The literature [14] has reported that the electrode surface modified by silver nanoparticles can be used in the detection of hydrogen peroxide. Compared with nanoparticles, three-dimensional nano-porous films have a better spatial structure and higher electrical conductivity. Therefore, NPSFs are deemed to have tremendous application potential to be non-enzyme hydrogen peroxide sensor.

In the present work, magnetron co-sputtering was chosen to prepare the precursor films. This technique provided high sputtering rate and contributed to obtain a uniform composition distribution [15]. Besides, the alloy composition can be easily controlled by the sputtering power. The vapor–solid quenching during sputtering provided the enough cooling rate to form metallic glass or nanoparticles phase and to achieve a fine morphology. In the next step, chemically dealloying method was used to form nano-porous structure. Then we studied the application of nano-porous silver films in the detection of hydrogen peroxide.

2. Experimental procedure

2.1. Fabrication of nano-porous silver films

The precursor films of different compositions were deposited on silica glass substrates via magnetron co-sputtering. The films

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consisted of three elements: silver, magnesium and cerium. In order to obtain a better morphology, the rare earth element (cerium) was added to improve glass forming ability of the films. All the targets were prepared by pure ingots (99.99% Ag, 99.95% Mg and 99.9% Ce). The compositions of the as-deposited films can be adjusted by utilizing different powers for each target. The distance of each target to the substrate was 120 mm. The base pressure of the chamber was pumped down to less than 4.0×10^{-3} Pa. All the experiments were performed at room temperature and water-cooling system was adopted to avoid the substrate temperature too high.

When sputtering completed, the precursor films were put into pre-made etchant solution at 298 K for chemically dealloying. The etchant solution was 0.1 mol/L H_2SO_4 and the corrosion time was set as 90 min. After rinsing in deionized water for a couple of times, nano-porous silver films were made into electrodes, then dried and stored in drying oven for later use. The electrode size was prepared as 1 cm \times 1 cm.

2.2. Characterization and electrochemical measurements

X-ray diffraction (XRD) and high resolution electronic microscope (HRTEM) were used to identify the structure of precursor films. X-ray diffraction was performed at 40 kV and 40 mA using Cu K_{α} radiation. Samples for HRTEM were deposited on copper grids by in situ sputtering, which was beneficial to obtain original information about the films and avoid the impact of ion thinning. Scanning electron microscope (SEM) was employed to observe the surface morphology of the precursor films and NPSFs. The operating environment was in high vacuum and the acceleration voltage was 15 kV. Energy dispersive spectroscopy (EDS) was used to detect the composition of the samples.

Cyclic voltammetry (CV) curves were collected with an electrochemical workstation. The electrochemical experiments were conducted in a three-electrode electrochemical cell, including a saturated calomel electrode (SCE) as the reference electrode, a Pt plate as the counter electrode and a nano-porous silver film as the working electrode. Phosphate buffer solution (PBS) was chosen as the supporting electrolyte to avoid excessive decomposition of the hydrogen peroxide to water and oxygen. A Constant water bath pan was used to keep the temperature stabilized at 25 °C. The experimental procedure was as follows. Before each experiment, supporting electrolyte was deoxygenated by bubbling with 99.99% nitrogen for 15 min. Then the electrode surface was rinsed by deionized water and subsequently subjected to 5 cycles in proper potential range before collecting the actual data. The scanning rate was set to be 50 mV/s using 0.1 M/L PBS (pH 7).

3. Result and discussion

3.1. Structural characterization

In this study, we investigated the influence of the alloy composition on the microstructure. Silver content was chosen as the variable parameter. With increasing silver content, the microstructure and morphology of the samples revealed an obvious evolution. Fig. 1 depicts the XRD patterns of precursor films with different silver content. It shows that $Ag_{65}Mg_{24}Ce_{11}$ and $Ag_{76}Mg_{16}Ce_8$ possess broad diffraction peaks, implying that a metallic glassy structure formed in the films, while $Ag_{88}Mg_9Ce_3$ reveals relatively sharp diffraction peaks.

The SEM images of the precursor films clearly reveal the evolution of the morphology. From Fig. 2a and b, it can be observed that the film surface demonstrates a hierarchical structure, consisting of smaller grains. Most of the particles are oval shape and a few particles are triangular shape. So they achieve random but relatively

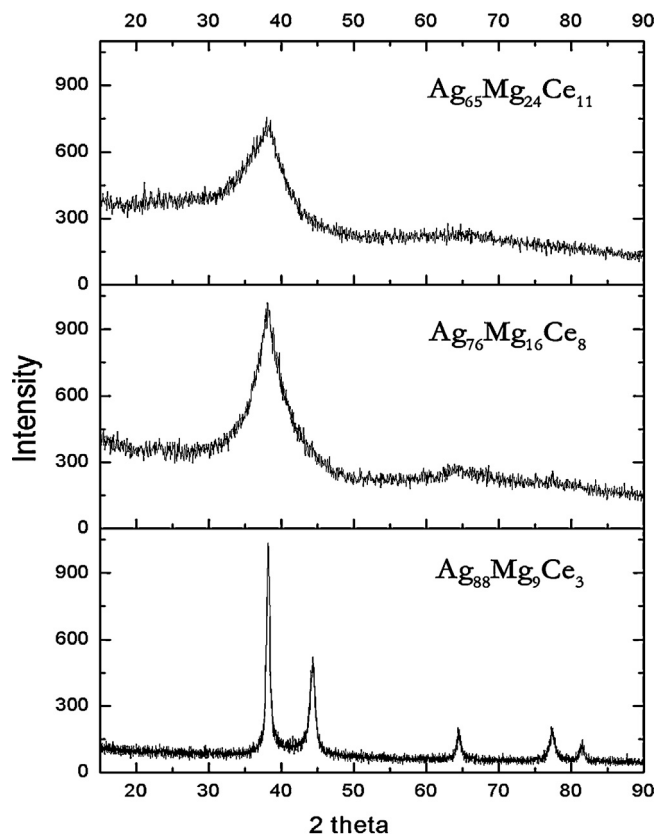


Fig. 1. The XRD patterns of precursor films. With increasing silver element, the patterns exhibit an obvious evolution.

dense packing with interconnected interfaces. The average size of the particles is about 25 nm. With increasing silver content, the particles gradually grow and became the shape of multi-angular, as shown in Fig. 2c–e, which indicated that the increasing silver content can promote the aggregation of clusters.

Fig. 3 shows the TEM patterns of the initial stage of the thin films. From the selected area diffraction patterns, it is believed that the films contain glassy region and AgMg nanoparticles. Additionally, the bright field image of the specimen reveals that AgMg nanoparticles embed in the glassy matrix. The formation process of the composite structure can be described as follows. Firstly, the energetic Ar ions were generated in glow-discharged plasma and bombarded the targets surface to cause the removal of the targets atoms [16]. Then the secondary electrons were also emitted from the target surface as a result of the ion bombardment [17,18]. In the process of the atoms sputtered to the substrate, some of them collided to form clusters in the chamber. These clusters became independent cores when they arrived at the substrate. In the next step, the relaxation and diffusion process followed the atomic collision cascade that triggered by sputtering. Highly energetic atoms should somehow relax toward equilibrium, but significant atomic motion still continued, which favored clustering on the substrate surface. Due to the fast cooling rate, only a few clusters can achieve the thermodynamic equilibrium state. So, the nanoparticle structure was preserved.

After dealloying treatment, the product that produced by $Ag_{65}Mg_{24}Ce_{11}$ film exhibited the best morphology. Thus, the nanoporous film that fabricated from $Ag_{65}Mg_{24}Ce_{11}$ film was chosen for further exploration. Fig. 4(a) and (b) shows the top-view and cross-section SEM images of the film. The figures reveal that when Mg and Ce were dealloyed from the film, the residual Ag atoms self-assemble into a uniform three-dimensional porous structure

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