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Nanoporous gold for amperometric detection of amino-containing compounds

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ABSTRACT

Nanoporous gold thin films were prepared by electrochemical dealloying of Si out of Au_xSi_{1-x} co-deposited on Si substrate. The x values were easily controlled in the range of 0.1–0.9 by the distances between the sample position and the target positions at a constant plasma power. Structure of pores and gold ligaments could be controlled via adjusting the alloy compositions. The gold nanoporous films were applied for amperometric sensing of phenylamine (aniline) and hydroxylamine. It was found that the sensitivity of the nanoporous gold films was correlated with their porosity. Furthermore, nanoporous gold films with roughness factor of around 25 provided high sensitivity, good repeatability, relatively low detection limit and good resistance toward electrode fouling as compared to other electrodes in the literature. These achievements offer a simple method for nanoporous gold films which exhibit stable performance in environmental monitoring.

1. Introduction

In recent years, nanoporous gold (NPG), possessing a high surface area, good conductivity and tunable porosity, has attracted much attention owing to their promising applications in various fields. In order to fabricate NPG structures, electrochemical dealloying or selective etching is considered as a simple and effective approach. Successful fabrication of NPG has been reported by dealloying one less noble component such as Ag, Cu, Ni, Pd, Zn out of suitable precursor alloys [1,2]. On the other hand, thin films of NPG fabricated from Au_xSi_{1-x} systems were once reported to provide more advantages such as good uniformity, well-controlled porosity and thickness, feasibility of handling and crack-free films [3].

There were a significant number of studies on application of NPG in catalysis, sensors, actuators and biofuel cells. Recent research trend has focused on the possibility of using NPG for electrochemical detection of pollutants and toxic substances such as nitrite, p-nitrophenol and hydrazine [1]. Also, it was mentioned that the oxidation or reduction of these substances over NPG are importantly attributed to the function of OH^- and NO_2^- groups [1,4]. These results have offered a great impetus for further research and development of NPG for sensing of other pollutants in the field of environmental monitoring.

Amino-containing compounds such as hydroxylamine and phenylamine (aniline) often attract great concerns due to their wide utilization associated with arising environmental problems. Aniline and some of its derivatives play an important role in industrial activities including the production of urethanes, intermediates for herbicides and other pesticides, dyes and pigments, accelerators and antioxidants for the rubber industry [5]. However, aniline creates severe health problems such as anoxia, erythrocyte damage, spleen effects and is also considered as a suspected carcinogen [1,6,7]. For these reasons there have been numerous studies aiming to develop reliable methods for aniline detection. Several analytical procedures have been proposed, including spectrophotometry, NIR spectrometry, gas chromatography, capillary electrophoresis, and high-performance liquid chromatography (HPLC) [6]. Although electrochemical sensing is a simple and convenient way to detect a wide range of chemicals, the application of this technique for aniline determination is still difficult due to the fact that the surface of glassy carbon and noble metal electrodes are easily deactivated as a result of irreversible adsorption of polymeric reaction products [6,8]. The task of developing good sensing electrodes for aniline is necessary but still quite challenging. Hydroxylamine is a well-known mutagen, moderately toxic to humans, animals, and plants [9]. It is a kind of reducing agent and raw material in industry and pharmacy. There are a number of electrodes employed for amperometric detection of hydroxylamine [9–13]. However, studies are still needed achieve reliable, reproducible, and highly sensitive materials for detection of hydroxylamine with low detection limit

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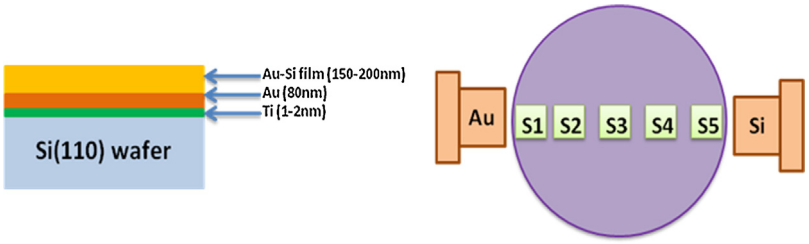

Fig. 1. (a) Schematic of sputtered Au–Si films and (b) top view of sputter positions for the S1–S5 films.

and wide detection range for industrial, environmental monitoring, clinical diagnostic as well as biological processes.

In this study, in an attempt to develop NPG thin films for environmental monitoring, we examined the formation of NPG thin films by dealloying of Au_xSi_{1-x} films and investigated the performance of those NPG thin films in amperometric sensing of phenylamine and hydroxylamine.

2. Experimental

2.1. Codeposition of Au and Si

By sputter deposition in a vacuum chamber working at a base pressure of 10^{-6} Torr, Au_xSi_{1-x} thin films were formed on n-doped Si(1 1 0) substrates (1 cm × 2 cm) with 5 nm Ti adhesion layer and 30 nm Au layer etch stop (Fig. 1a). The thickness of the deposited films was around 100–150 nm. By applying the fixed plasma power (10 W for Au and 200 W for Si), Au_xSi_{1-x} films with different compositions ($0.1 < x < 0.9$) were obtained by varying distances between the sample positions and the Au and Si targets. Sample positions were labeled S1–S5 (Fig. 1b). A bare Au electrode ($x = 1$, thickness of 150 nm) as a reference electrode was also prepared using an Au target only. Depth profiles of the film compositions were measured by Auger Electron Spectroscopy (AES) (PHI-700, Ulvac-PHI). The films were vertically etched by a constant 3 kV Ar ion beam while being depth profiled by a 10 kV electron beam. The sputter time was proportional to the depth into the films.

2.2. Dealloying

Si was electrochemically etched out of Au_xSi_{1-x} films in 3% HF aqueous solution [3,14]. For each sample, the bottom Si(1 1 0) substrate was sealed with silicone glue before being exposed to electrochemical processes. The middle part of the top Au_xSi_{1-x} surface was also sealed, exposing an 1 cm × 1 cm area on the right for dealloying/sensing and the remaining left area for electrical connection. After sealing, the exposed area on the right was immersed in the HF solution and dealloyed by applying a linear potential sweep from 0 V to 1.3 V with a scan rate of 10 mV s^{-1}. A representative etching curve is shown in Fig. 2. Linear potential sweeps were applied for dealloying because a gradual potential increase was better than a step function for avoiding cracks and surface damages in the thin films during dealloying. When the scan rate was too high, instabilities occurred in NPG films in subsequent cleaning and roughness factor measurements. We suspect that the instability was due to not enough time for the remaining gold atoms to diffuse around to form stable pores [1]. Also, pores will be very small with high scan rate. In this regard, lower scan rate is preferred to have stable and fully developed pores. However, when the scan rate was too low, it took unnecessarily long time to prepare NPG films. 10 mV s^{-1} was turned out to be an appropriate rate to prepare stable NPG films with reasonable preparation time.

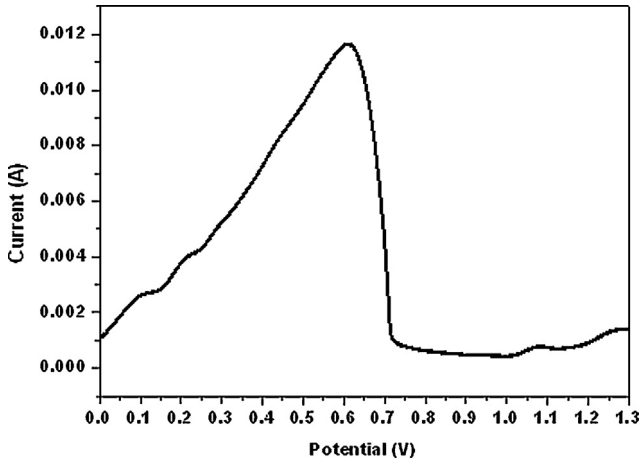

Fig. 2. Linear potential sweep during dealloying of Au–Si films.

2.3. Electrochemical experiments

All electrochemical measurements were carried out in a three-electrode system with Ag/AgCl (3 M KCl) as reference electrode, Pt wire as counter electrode, and NPG films as working electrodes in an electrochemical analyzer (CH660, CH Instruments Inc.). Before each electrochemical experiment, the NPG thin films were cleaned in 1.5 M H_2SO_4 solution using cyclic scan from −0.25 V to 1.8 V (vs Ag/AgCl) with the scan rate of 100 mV s^{-1} until obtaining reproductive voltammograms. The charge passed during reduction of gold oxides was calculated by integration of the gold oxide-stripping peak of these curves. A conversion factor of 450 μC cm^{-2} was used to calculate the roughness factor [15]. Phosphate buffered saline (PBS) solution containing 0.15 M NaCl with pH 7.2 was used as supporting electrolyte for electrochemical sensing. Amperometric detection of phenylamine and hydroxylamine were conducted in a glass cell containing 10 ml PBS by successive adding of the analytes at room temperature. All the current values were measured on NPG films with the same 1 cm × 1 cm exposed area. Therefore, all the current values in the experimental results are in fact current densities (current/cm^2).

2.4. Materials

H_2SO_4, phenylamine, hydroxylamine (all from Sigma-Aldrich), HF (J.T. Baker) were used without purification.

3. Results and discussion

3.1. NPG thin film preparation

The Au_xSi_{1-x} films of $0.1 < x < 0.9$ were co-sputter deposited on Si substrates. To investigate the effect of the alloy composition on structural evolution and related electrocatalytic behaviors, alloy films with five different compositions were prepared, designated