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Effect of annealing atmosphere on the thermal coarsening of nanoporous gold films

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ABSTRACT

The coarsening of nanoporous gold (NPG) is significantly influenced by surface adsorbates at elevated temperature. In this paper, the effect of annealing atmosphere on the thermal growth of the porous structure was investigated by scanning electron microscopy and X-ray photoelectron spectroscopy. The NPG films were annealed in oxidative (air), inert (Ar) and reductive (CO) atmospheres at 100–600 °C for 2 h, respectively. The experimental results indicate that the NPG films show the best stability in the reductive atmosphere and the worst thermal properties in oxidative air. The NPG films annealed in air exhibit a significant pore growth at 200 °C and lose the porous structure at 300 °C, while those annealed in CO gas at 600 °C still remain the porous network. The thermal-induced coarsening of NPG films in air can be attributed to the desorption of O_2 from the NPG surface above 200 °C. In contrast, the stabilization of the NPG films in CO gas originates from the strong binding of CO with Au atoms to form a complex adsorption layer, which effectively inhibits the surface diffusion of Au atoms.

1. Introduction

In recent years, nanoporous gold (NPG) has attracted considerable interest, fueled by its potential application in various fields, such as sensors [1,2], actuators [3], catalysts [4,5], and supercapacitors [6]. All these remarkable properties of NPG originate from a special sponge-like structure, characterized by bicontinuous pores and ligaments both in nanoscales. However, a critical issue limiting the applications of NPG is the thermodynamically unstable structure, which is prone to coarsening at elevated temperatures [7–9]. It is well known that the thermal-induced coarsening of nanoporous structure has a harmful effect on the mechanical, chemical, and physical properties [10,11]. For example, the NPG annealed in N_2 at 200 °C exhibited an increase of ligament from 12 to 30 nm in length scale, and correspondingly, the catalytic activities were degraded [12,13]. Therefore, it is crucial to investigate the thermal coarsening of NPG materials.

Coarsening of porous materials is typically ascribed to surface diffusion. Thus, one would expect that the stability of NPG is strongly affected by the surface adsorbates [14–16], since the adsorbed species, such as oxygen, ozone, and carbon monoxide, can modify the surface diffusion. Biener et al. [15] demonstrated that the surface chemistry could control the coarsening kinetics of NPG annealed in inert He and reactive O_3 environments. They found that the ligament size of NPG increased from 30 to 90 nm in He environment at 450 K, while conserved in reactive O_3 environment below the desorption temperature of oxygen (500 K). Recent discoveries showed that the Au thin films annealed in N_2 and Ar atmospheres exhibited an obvious grain growth, whereas those annealed in forming gas (mixture of CO and Ar) preserved the initial grain size [16,17]. Due to the fact that the interaction of adsorbates with surface Au atoms differs with the types of gas species, it seems likely that the growth rate or mechanism will depend on the annealing atmospheres. However, the effect of annealing atmosphere on the thermal stability of the NPG films is still poorly explored.

In this paper, we perform a systematically thermal characterization of the NPG films under a series of environment-controlled annealing experiments to develop a fundamental relationship of surface adsorbates with the stabilization of NPG materials. Specifically, we aim at determining the structural evolution and the growth kinetics of NPG films annealed in oxidative (air), inert (Ar), and reductive (CO) atmospheres. On the basis of the kinetics data, we discuss how the adsorbates control the pore growth of the NPG films.

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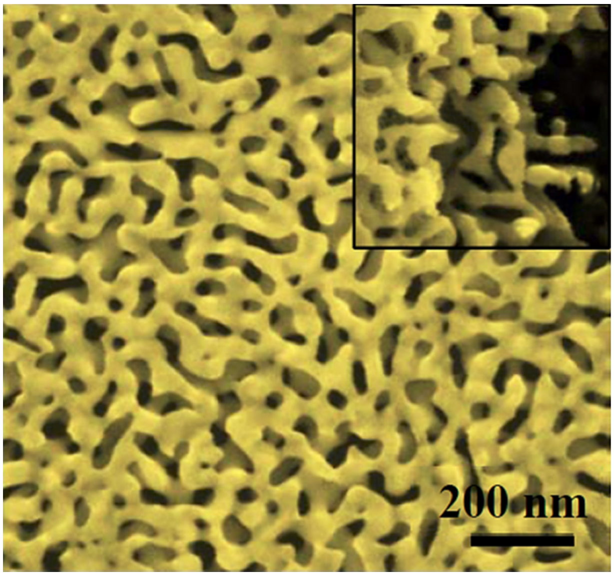

Fig. 1. SEM image of the as-prepared NPG film. The inset is the cross-sectional SEM morphology with the same scale bar.

2. Experimental procedure

White gold ($Au_{35}Ag_{65}$ in at%) films with a thickness of 100 nm were used to fabricate the porous structure through chemical dealloying. The white gold films were floated in the concentrated HNO_3 (65% in wt%) for 10 min at 20 °C, and then washed by distilled water. The as-fabricated NPG samples (5 mm × 5 mm) on Si wafers were placed into a quartz boat and annealed in a quartz tube resistance furnace under the atmospheres of oxidative air (O_2), inert Ar and reductive CO gas (5% CO + 95% Ar), respectively. The gas flows of the inert Ar and reductive CO gas were both 20 ml/min. Thermal treatments were performed at 100–600 °C for 2 h. The heating rate was set at 10 °C min^{-1}, and furnace cooling to room temperature.

The surface topography was observed by an FEI Quanta 450 field-emission scanning electron microscopy (SEM). The feature size, including the sizes of ligament and surrounding pore, was estimated from the SEM images. MATLAB was used to quantitatively analyze the area fraction of the pores according to SEM images [18]. Composition and oxidation state of the NPG samples were analyzed by X-ray photoelectron spectroscopy (XPS, Phi V5000) with an Al K_a X-ray source.

3. Results

3.1. Surface morphology

SEM image of the as-prepared NPG film is shown in Fig. 1, which displays an irregularly sponge-like structure. The cross-sectional SEM image (inset in Fig. 1) indicates that the ligaments and pores are both interconnected inside, forming a three-dimensional (3D) porous structure. The average sizes of pore and ligament are 15 and 35 nm, respectively, estimated from the surface SEM images.

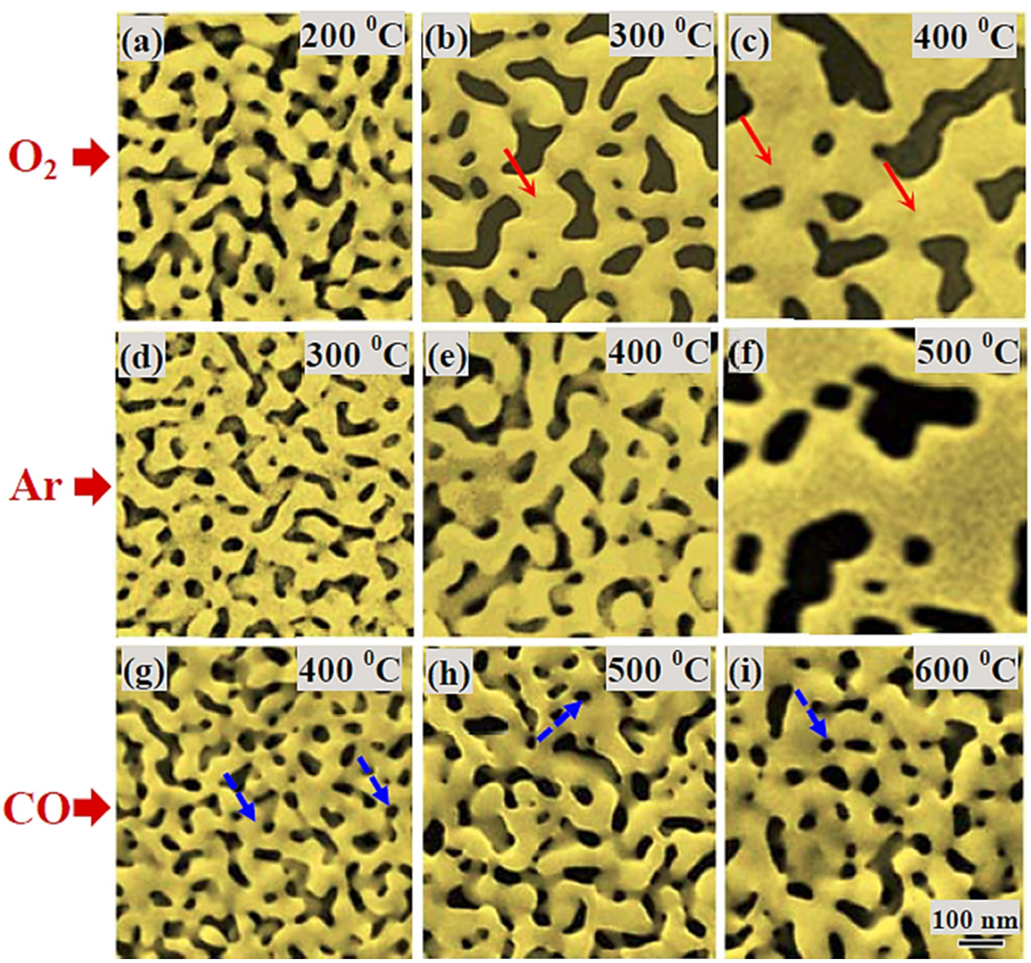

Fig. 2. SEM images of the NPG films annealed at different atmospheres for 2 h. (a–c) Annealed at 200, 300, and 400 °C in O_2, respectively; (d–f) annealed at 300, 400, and 500 °C in Ar, respectively; (g–i) annealed at 400, 500, and 600 °C in CO, respectively. All SEM images have the same scale bar.