Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 61 (2009) 1125–1128
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Effects of substrate curvature on dealloying of nanoporous thin films

Wen-Chung Li and T. John Balk*

Department of Chemical and Materials Engineering, University of Kentucky, 177 F. Paul Anderson Tower, Lexington, KY 40506-0046, USA

Received 26 August 2009; revised 1 September 2009; accepted 3 September 2009
Available online 6 September 2009

Co-sputtered AuPdAg alloy films on flat and curved substrates were investigated to determine the effects of substrate curvature on dealloying and microstructure of nanoporous (np) AuPd. Ligament morphology, film cracking and composition were significantly different for np-AuPd in concave vs. convex film regions. Convex substrate curvature led to extensive film cracking, wide and high aspect ratio ligaments, and low residual Ag content. This is attributed to a more tensile stress state that enhances the dissolution rate of Ag.

Keywords: Dealloying; Nanoporous; AuPd; Substrate curvature

Dealloying is a straightforward process for producing a nanoporous (np) material by selectively dissolving one or more metallic components from a precursor alloy. Typically, the less noble component is etched from the alloy with a strong oxidizing acid, and the remaining, more noble atoms undergo surface diffusion and agglomeration to form an interconnected network of ligaments with open porosity [1]. The typical length scale for pores and ligaments in np metals is ~2–10 nm. A range of np metals has been investigated in bulk form, as thin films, or as nanostructured materials, including np-Au [2–4], np-Pd [5,6], np-Cu [7] and np-Ni [8]. In addition, AuPd alloys have been investigated as materials for biocoating [9], hydrogen sensing [10–13] and catalysis [14,15]. Such applications require high surface area for improved performance, and thus np-AuPd thin films would offer excellent chemical and structural properties for these areas.

Two primary mechanisms, namely surface dissolution and surface diffusion, operate during the dealloying process and can significantly affect the final np structure. Several aspects of nanoporosity formation and its relation to processing parameters have been investigated. For example, temperature of the dealloying etchant affects the pore/ligament size of np-Au [16]. Crack-free thin films of np-Au on Si substrates can be achieved using a two-step dealloying method [17]. In addition, electrolyte concentration and film stress may play a significant role in determining dealloying rate and final np structure. There are many potential factors that can influence both surface dissolution of the less noble alloying element and surface diffusion of the more noble element, thereby shifting the dealloying stages dominated by each mechanism. The results presented here suggest that substrate curvature is also a critical factor for dealloying rate and the np structure that evolves. This aspect has not been investigated before, but is important to the fabrication of np metal films on irregular and nonplanar substrates, which may be important for application of these novel materials.

In this study, thin films of a AuPdAg alloy were deposited on flat single-crystalline (1 0 0)-oriented Si (380 μm thick, CrysTec GmbH, Berlin, Germany) as well as on curved Kapton sheet (50 μm thick polyimide, DuPont Kapton, type 200 HN) by co-sputtering Au, Pd and Ag. Film deposition was performed by magnetron sputtering (ORION system, AJA International Inc., North Scituate, MA, USA). The base pressure of the sputtering system was 1.3×10^{-6} Pa (1.0×10^{-8} torr). Both substrates were coated with a 10 nm Ta interlayer prior to deposition of the 70 nm AuPdAg alloy film, to improve adhesion to the substrate. As-deposited films were dealloyed via free corrosion (no applied potential) in diluted nitric acid (35 vol.%) for 45 min at room temperature, then rinsed several times and soaked in ethanol (95% purity) for 15 h before characterization.

Composition of the as-deposited AuPdAg alloy film was 20.3 at.% Au, 7.0 at.% Pd and 72.3 at.% Ag, as measured by energy dispersive X-ray spectroscopy (EDS) in

* Corresponding author. Tel.: +1 859 257 4582; fax: +1 859 323 1929; e-mail: balk@engr.uky.edu

1359-6462/$ - see front matter © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2009.09.003

a scanning electron microscope (SEM, Hitachi S3200). This composition was consistently measured at all film locations on both flat and curved substrates. Texture of the as-deposited film was determined by X-ray diffraction (XRD, Siemens D500) and consisted only of a strong (1 1 1) component. Microstructure of the alloy and np-AuPd films was characterized with a Hitachi S900 SEM, operated at 3 kV in secondary electron mode. Initial attempts at dealloying of the flat AuPdAg alloy film resulted in nonideal compositions: after 30 min dealloying time, too much Ag (>35 at.%) remained in the film, while after 60 min dealloying time, nearly all Pd had been removed (<1 at.% final Pd content). In order to minimize the remnant Ag and maximize the Pd content in the np film, a dealloying time of 45 min was used in this study. Final composition of the film on curved substrate was dependent on local curvature.

Figure 1 shows the morphology of the as-deposited AuPdAg film and the dealloyed np-AuPd film on a flat Si substrate. Grains in the as-deposited film ranged in size from 15 to 25 nm. After dealloying, the flat film exhibited fine pores and ligaments with an average diameter of 15 nm, close to the size of grains in the as-deposited film (compare Fig. 1a and inset of Fig. 1b). A number of cracks, 10–25 nm wide and ~100 nm long, were observed throughout the np-AuPd film. Lu et al. reported that 30 at.% of the more noble constituent (Au in their case) is needed to prevent crack formation in np thin films on flat substrates [18]. Sun et al. also reported an optimal composition of the precursor alloy (30 at.% Au and 70 at.% Ag) for producing crack-free np-Au films on Si [17]. Thus, cracking of the np-AuPd film in the current study may result from too little Au/Pd (27.3 at.% total) in the precursor alloy. Furthermore, although Pd is more noble than Ag, it dissolves slowly in nitric acid, leading to significant Pd loss at long dealloying times. After 45 min dealloying time, composition of the np-AuPd film on flat Si substrate was 87.6 at.% Au, 4.2 at.% Pd and 8.2 at.% Ag. By comparing the relative amounts of Au and Pd before and after dealloying, and assuming that no Au is lost during dealloying, it is calculated that 77% of the initial Pd content was lost during dealloying. This significant Pd loss reinforces the idea that crack formation in the dealloyed film is due to a low noble metal content, as the amount of Au plus remnant Pd accounts for only 22 at.% of the initial film composition.

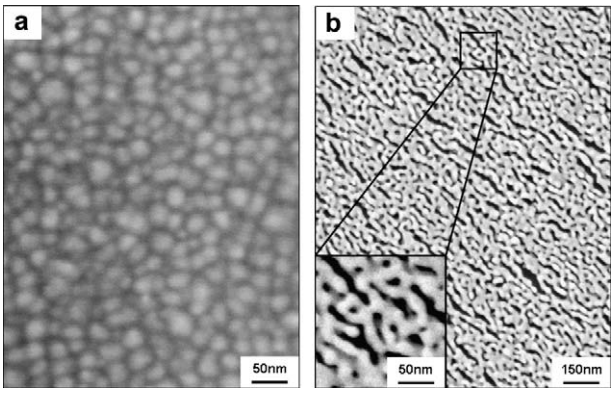

Figure 1. Morphology of (a) the as-deposited AuPdAg alloy film and (b) the dealloyed np-AuPd film on Si substrate. Grain size in the as-deposited film was 15–25 nm. The np-AuPd film exhibited ligaments and pores with an average size of 15 nm. A number of cracks, 10–25 nm in width and ~100 nm in length, appeared in the dealloyed np-AuPd film.

For the np-AuPd film on curved Kapton substrate, the distribution and geometry of cracks as well as the final np structure varied considerably as a function of local substrate curvature. During film deposition and dealloying, the Kapton substrate was held in a curved shape by a polymer template (high-density polyethylene, HDPE). The top surface of the HDPE template was corrugated, with periodic ridges that were 2 mm high and round at the top. The radius of curvature at the top of each ridge was 0.5 mm, and center-to-center distance between neighboring ridges was 3 mm, i.e. the gap between ridges was 2 mm. The Kapton substrate was placed between two templates with this shape, and these templates were then squeezed together to induce periodic curvature in the Kapton. The substrate remained clamped in this manner for 20 min, after which one template was removed to expose the Kapton for film deposition. The substrate retained the periodic, corrugated shape. Both the HDPE template and Kapton sheet were resistant to corrosion in the nitric acid solution, allowing the corrugated Kapton sheet to remain fixed on the bottom template, with no change in curvature during deposition, dealloying and subsequent rinsing/cleaning. For SEM and EDS characterization, the np-AuPd film on corrugated Kapton was carefully removed from the template, cut into small pieces (2 mm × 4 mm), and then affixed to a flat sample holder using colloidal graphite paint at one corner. Care was taken to prevent the Kapton from flexing during the cutting and mounting process. It appears that no significant flexing occurred, as the np-AuPd film did not exhibit a deformed ligament morphology. Moreover, the cracking patterns at various locations of the film are the opposite of what would be expected if the Kapton substrate had flexed and caused cracks in the film (see discussion below).

Cracking at different locations in the curved np-AuPd film is shown in Figure 2. The distance between the valley (point A) and the ridge (point E) was approximately 4 mm. Note that this is the distance along the substrate surface, not the half-width of the periodic distance between template ridges. SEM micrographs were taken at intervals of 1 mm between adjacent points A–E. The substrate curvature at points A (concave)–E (convex) varied between 1.48, 1.23, 0, −0.91 and −1.51 mm^{-1}, respectively. These values were measured from a cross-sectional image of the corrugated Kapton sample (shown in the image at the center/bottom of Fig. 2). Each micrograph in Figure 2 consists of two images taken at the same location, but at high vs. low magnification (on the left and right, respectively). Low-magnification images of the np-AuPd film in the concave region (points A and B) revealed few cracks, while the flat and convex regions (points C–E) exhibited significant cracking. Additionally, beginning at point C, crack width increased as the substrate transitioned from flat to convex and cracks were apparent even at low magnification. The high-magnification images