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A thermal treatment approach to reduce microscale void formation in blanket nanoporous gold films

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This paper illustrates the effect of thermal treatment and alloy composition on the microstructures of gold–silver films and subsequently dealloyed nanoporous gold films. Even though thermal treatment of alloys increases tensile stress in gold–silver films, it mitigates the formation of microscale voids during dealloying. The voids in the dealloyed film are too large to be rationalized by relaxation of the residual stress. The interplay between volume shrinkage during dealloying, residual stress and thermally induced deformation is discussed to explain void formation.

Keywords: Porous material; Annealing; Residual stresses; Fracture; Dealloying

Nanoporous gold (np-Au) is an emerging material for use in various applications, notably in functional coatings used in implantable medical devices for controlled drug elution and increased cellular attachment. Several groups have utilized this material in sensors [1–3], fuel cells [4] and bioanalytical diagnostic platforms [5]. It is important to understand the fundamental properties of np-Au [6–10] and devise methods of reliable fabrication and integration in microdevices to realize its potential. Our group has previously demonstrated a technique to facilitate the integration of free-standing np-Au beams in microsystems by preventing tensile fracture during their production [7]. Blanket films suffer from similar crack-like void formation, therefore limiting their utility as coatings [11]. A limited number of approaches have been demonstrated to produce "crack-free" np-Au films [12,13]. In this paper, we illustrate that thermal treatment of alloy films reduces subsequent microscale void formation during the dealloying step that leads to np-Au films. The central observation is that heat-treated blanket gold–silver (AuAg) films develop larger tensile stresses, yet when dealloyed, surprisingly lead to a np-Au film with reduced cracks. We discuss underlying mechanisms that may lead to this phenomenon.

Blanket AuAg films of three different compositions were prepared by simultaneously sputtering gold and silver targets. For each composition, a set of four 50 mm diameter silicon wafers were sputter-coated. In order to prevent film delamination, wafers were initially coated with 20 nm thick chrome and 20 nm thick gold. Following the Cr/Au deposition, without breaking the vacuum, the gold target gun power was kept at 100 W and the silver target gun power was switched to 150, 200 and 250 W to obtain various alloy compositions. The nominal film thickness of 900 nm was obtained by varying the deposition time. The alloy films (on the substrate) were subjected to a thermal treatment protocol to systematically modify the microstructure and stress-state. Each sample of different composition was either left as-deposited, or annealed at 150 or 300 °C. The thermal treatment step was performed with an AXIC, Inc. As-One rapid thermal processor (RTP) in nitrogen at atmospheric pressure. The temperature ramp rate was 20 °C s^{-1}, and the sample was removed from the RTP after 4 min of cooling when the temperature dropped below 50 °C. Each wafer was held at the target temperature for 10 min. The samples were later dealloyed in concentrated (65%) nitric acid at 85 °C for 10 min, sub-

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sequently rinsed in deionized water and dried under nitrogen. Energy-dispersive spectroscopy of the dealloyed samples revealed less than 4 at.% silver in np-Au films.

Several thin film characterization methods were employed after each main process step (i.e. deposition, annealing, dealloying). Film thickness was measured with a Dektak 8 profilometer using a low stylus force of 10 μN. The wafer curvature due to film stress was measured with a Frontier Semiconductor Inc. FSM-8800 scanning laser wafer curvature measurement system, and the residual stress was extracted as outlined in our earlier work [10]. The effect of the Cr/Au adhesion layer was removed during the residual stress calculations [10]. The microstructure of blanket films was examined by scanning electron microscopy (SEM) with a Zeiss FESEM SUPRA 40, while the alloy composition was characterized using an energy dispersive spectroscopy instrument attached to this electron microscope. The root-mean-squared (RMS) roughness of the alloy surface was examined by a Veeco white light interferometer (WLI). Digital image analysis of the micrographs was performed to quantify percentage coverage and average area of the cracks and pores, using the techniques described in Ref. [10].

Table 1 summarizes the alloy composition, and film thickness before and after dealloying for each three alloy composition sets. Annealing did not have a detectable effect on the alloy film thickness (data not shown). However, film thickness decreased after dealloying, with larger decreases for larger silver content (i.e. by 3.8%, 4.4% and 12.3% for sample sets A, B and C, respectively). The reduction in film thickness is most likely due to volume shrinkage during dissolution of silver [10,14]. Figures 1 and 2 illustrate the microstructures of annealed blanket alloy films and the subsequently dealloyed films, respectively. Thermal treatment at 150 °C does not lead to noticeable changes in alloy microstructure; however, treatment at 300 °C leads to grain growth, particularly in films with a higher silver content. Thermal treatment of the alloy had a pronounced influence on the microstructure of subsequently dealloyed films. The percentage coverage and average area of major cracks increased at 150 °C and decreased at 300 °C, based on digital image analysis of micrographs (Fig. 3A). Increased silver content in the alloy led to even more dramatic crack coverage and average crack area, while the trend with annealing temperature persisted regardless of silver content. For sample set C (the highest initial silver content), crack-like voids were mostly interconnected, unlike the sample sets A and B. Micrographs of np-Au film cross-sections for "as-deposited" samples show that the microscale voids traverse the thickness of the film down to the substrate (Fig. 3B). Since these voids traverse the entire thickness of the film, they remove the residual stress in all np-Au films (except crack-free sample A pre-treated at 300 °C) to levels undetectable by the wafer curvature measurement apparatus, as shown in Figure 4. Cross-sectional views also demonstrate relatively homogeneous porosity in islands in the film.

A quick analysis of the percentage dimensional change extracted from the ratio of crack width to the island width predicts a planar contraction of between 6% and 24% across different samples. These dimensional changes are comparable to ones that can be obtained by doubling the percentage shrinkage in film thickness – the film has only one degree of freedom out-of-plane, while it has two degrees of freedom in-plane. The percentage change in film thickness is higher for samples with higher initial silver content. Similarly, the percentage coverage and average microvoid area are also higher for samples with higher initial silver content. In addition, despite the insensitivity of residual stress in alloys to the initial silver content, a dramatic enlargement of crack-like voids are visible for samples with higher initial silver content. Hence, it is likely that the dimensional change due to volume shrinkage is dominant over the changes due to heat treatment.

That said, heat treatment clearly affects microvoid formation, as illustrated by the suppression of void formation at elevated temperatures. Ignoring for the moment the possibility of stress-driven morphology evolution, one possibility is that the void formation is controlled by microstructural defects that are mediated by heat treatment. Generally, the small microvoids (in terms of area and density) are observed for samples that exhibit grain growth, suggesting the possibility that heat treatment removes nanoscale voids that serve as nucleation sites for microscale crack-like voids. This is consistent with previous observations of buckled microbeams, which showed evidence of temperature-dependent condensation of nanovoids present in as-sputtered films [7]. The removal of defects via heat treatment may also be accommodated by compressive plastic strains induced at elevated temperatures [15]. If one assumes that the alloy yields in tension during cool down from deposition, the initial stress (without heat treatment) of ~100 MPa (see Fig. 4) implies compressive yielding at ~120 °C. Subsequent heating to 300 °C implies compressive plastic strains of ~0.2%. While reverse yielding during cool-down will decrease this value, it is much larger than the compressive strains of ~0.05% observed to decrease microvoid formation.

Another possible thermally activated mechanism is increased roughness of the alloy surface through anneal-

Table 1. Summary of measurements for the three main sample sets with different alloy compositions.

Sample name	Au content (at.%)	Ag content (at.%)	AuAg thickness (nm)	np-Au thickness (nm)
A	37.5 ± 0.6	62.5 ± 0.6	926.0 ± 22.8	898.5 ± 12.3
B	31.5 ± 0.3	68.5 ± 0.3	891.3 ± 15.8	858.7 ± 10.7
C	27.5 ± 0.4	72.5 ± 0.4	878.2 ± 19.9	788.6 ± 25.1

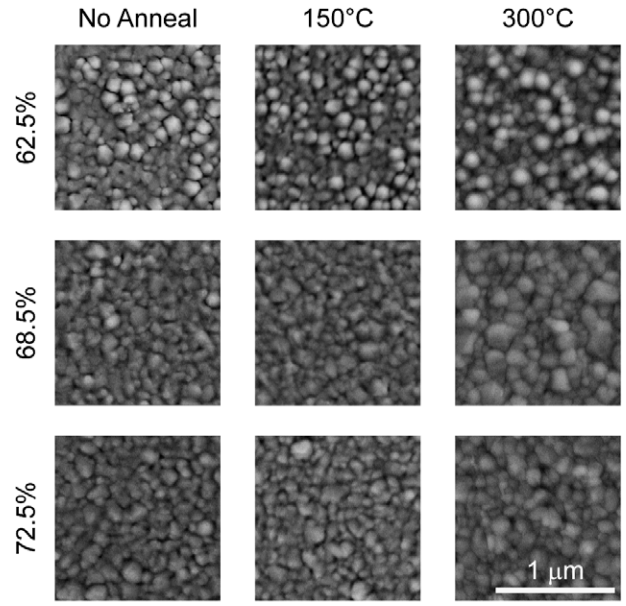

Figure 1. Micrographs of AuAg films (with various initial Ag content) after thermal treatment at different temperatures.

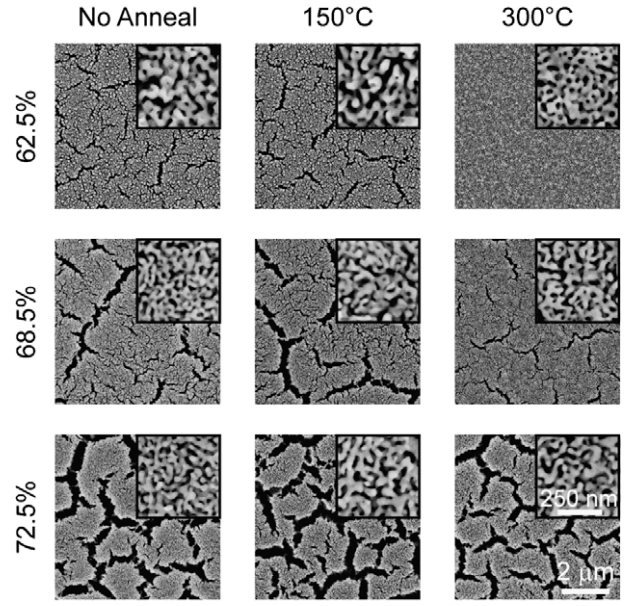

Figure 2. Micrographs of the np-Au films (with various initial Ag content) created by dealloying the thermally treated AuAg films. The larger images and the insets exemplify the typical crack formations and pore morphology, respectively.

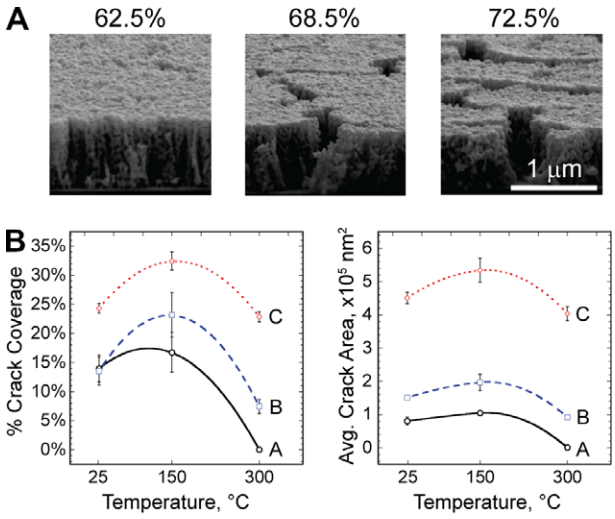

Figure 3. (A) Cross-sectional micrographs of the tilted np-Au samples (with different initial Ag content) obtained by dealloying "as-deposited" samples. (B) Percentage crack coverage and average crack area for three different initial Ag contents at various annealing temperatures.

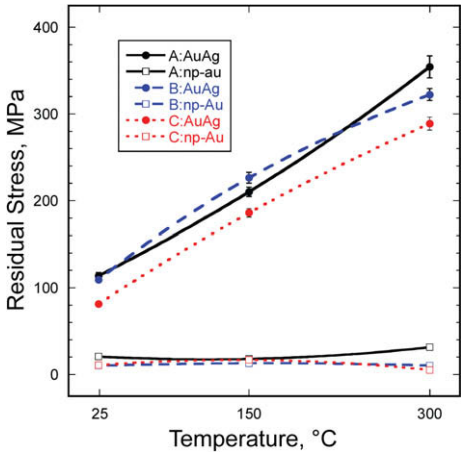

Figure 4. Residual stress in AuAg alloys after thermal treatment and subsequent dealloying. Curves are visual aids.

ing. The WLI measurements on the AuAg surface indicated that the RMS waviness of the surface remained comparable for different alloy compositions, while it followed the inverse nonmonotonic trend observed for crack coverage and average crack area in Figure 3B. Even though the WLI system does not provide meaningful information for the horizontal length-scale of roughness, its vertical resolution is good enough to make semiquantitative arguments about the alloys films. The RMS waviness of as-deposited films (including data from three alloy compositions) was 3.4 ± 0.7 nm, slightly decreased to 3.2 ± 0.3 nm for films at 150 °C, and finally increased to 3.8 ± 0.2 nm for films annealed at 300 °C. Despite the subtle changes, the surface roughening (much larger length-scale than changes in grain morphology observed by SEM) may play a role in the suppression of the lateral shrinkage of films during dealloying. It is plausible that the wavy film compensates for shrinkage.

The notion that morphological evolution is stress-controlled creates an interesting paradox: AuAg samples with the highest initial residual stress produce nanoporous films with smaller defects. While the apparent crack coverage and average area increased for samples annealed at 150 °C, there was a decrease in the crack-like void coverage and average area for samples annealed

at 300 °C. It seems clear that the stress influences the mass transport during dealloying process, as the microscale voids are too large simply to correspond to stress relaxation via film cracking. This conclusion is rationalized as follows: the relaxation of even the highest measured residual stress of ~350 MPa should only result in a strain of ~1–3% in blanket np-Au films, whose modulus is presumably in the 10-50 GPa range [10]. This implies that the islands (with sizes ~1–10 μm between crack-like features) would only retract 10–30 nm, which is much smaller than the observed width: hence, we use the term "crack-like voids", since it is unlikely the features are simply cracks driven by residual stress. A more plausible stress-based argument is that the higher initial stresses are (at least partially) associated with strain-hardening in the film: this might inhibit necking instabilities in ligaments formed during the dealloying step, and reduce the coalescence of nanovoids into microscale crack-like voids. This notion is supported in part by observations of necking in broken ligaments on either side of microscale voids [10], but considerably more work is needed to characterize void formation at various intervals of the dealloying process.

In conclusion, the best practice for making uniform nanoporous functional coatings under slight residual tension appears to be: (i) choosing an alloy composition near the parting limit of the AuAg alloy system (i.e. 60 at.% Ag); and (ii) annealing the alloy around 300 °C. It is likely that residual stress due to annealing has a negligible role in film cracking, and that volume shrinkage during dealloying is primarily responsible for crack formation in np-Au films. Thermal treatment at sufficiently high temperatures must suppress volume shrinkage, which in turn increases the uniformity and integrity of np-Au films.

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