Mitigation of tensile failure in released nanoporous metal microstructures via thermal treatment

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There is growing interest in freestanding structures of nanoporous metals for use in sensors, due to their increased surface area, compliance, chemical inertness, and biological compatibility.\textsuperscript{1,2} Despite the fact that well-established dealloying methods have been already developed for synthesizing nanoporous metals and thorough understanding of their electrochemical mechanism of formation has been achieved,\textsuperscript{3-7} there is currently a paucity of successful microfabrication technology for freestanding nanoporous microstructures. Of particular concern is the tensile failure of freestanding microbeams that occurs during the dealloying process. The existing techniques\textsuperscript{8-10} for developing nanoporous Au (np-Au) structures are limited in practical applications due to the difficulty of mechanical or electrical connection with other elements. In this letter, a fabrication technique to create freestanding np-Au bridges and cantilevers, based on microsystem microfabrication methods, is presented; failure is prevented by thermal treatments of the released microstructures prior to dealloying.

Figure 1 illustrates the fabrication process of a doubly clamped bridge. We started with \( p \)-type 100-oriented silicon as the substrate and used aluminum as the sacrificial material.\textsuperscript{11} Following standard chemical cleaning, an 80 nm SiO\(_2\) layer is thermally grown in wet O\(_2\) at 1100 °C. A 60 nm thick Al film is then deposited by sputtering. The bridge pedestal regions are lithographically patterned; the exposed Al layer is removed with Transene aluminum etchant and filled with sputtered Cr. Prior to depositing the Au–Ag alloy, a bilayer photoresist film (lift-off resist LOR 5B and positive photoresist AZ4210) is spun on and patterned, which produces a controlled degree of undercut on the bottom layer, preventing irregularities at the bridge edges after the lift-off process. The Au–Ag bridges (30/70 at. %) were created by cosputtering from Au and Ag targets, followed by lift-off in \( n \)-methyl-2-pyrrolidone. The Au–Ag alloy bridges were \(~\sim\) 750 nm thick as determined with a Wyko NT1100 optical profiler. Additional films of Cr (50 nm) and Au (500 nm) were deposited over the pedestal regions to reinforce the clamped ends and to prevent dealloying of the pedestals. The planarization of the Au–Ag alloy bridge shown in Fig. 1(a) can be achieved, by these techniques, within several

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FIG. 1. (Color online) Illustration of microfabrication method for freestanding np-Au bridge. (a) Schematic layout of a microfabricated Au–Ag alloy bridge with Al film underneath as a sacrificial layer. The bridge is secured by Cr/Au clamping films. (b) Release the bridge by successively etching the Al, SiO\(_2\), and Si. (c) Anneal at 250–400 °C for 10 min to induce thermal buckling. (d) Dealloy in nitric acid to create a flat freestanding np-Au bridge; remove rinse water by critical point drying.
nanometers. A KOH-based photoresist developer, AZ 400 K, was used to etch the sacrificial Al layer and release the bridges. Following the Al removal and rinse in de-ionized (DI) water, the underlying SiO₂ beneath the bridges was removed using a 10:1 DI:HF solution. The sample was again rinsed in DI water and etched for 1 h in a silicon etchant (30 wt % KOH and 5 wt % isopropanol in DI water) at 95 °C, which produced grooves approximately 25 µm deep [Fig. 1(b)].

To create the np-Au microstructures from the Au–Ag alloy bridges, the now released Au–Ag bridges were dealloyed in a 90 °C nitric acid solution (65%) for 10 min. The sample was then rinsed in DI water and etched for 1 h in a silicon etchant (30 wt % KOH and 5 wt % isopropanol in DI water) at 95 °C, which produced grooves approximately 25 µm deep [Fig. 1(b)].

The scale bars in Fig. 3a and b are 30 µm long.

The generation of tensile stress during the dealloying process is not fully understood at this time; here we focus on examining a thermal treatment protocol to mitigate tensile failure. To this end, a rapid thermal annealing (RTA) process was applied to the Au–Ag freestanding bridges prior to dealloying. It is important to note that RTA applied prior to the release step does not eliminate failure during the subsequent dealloying process, as expected. Pre-RTA at low temperature will neither release the deposition stresses nor, most importantly, build up any compressive residual strain, which may counteract tensile stress during the dealloying process.

To explore the effectiveness of thermal annealing in mitigating tensile stresses, the samples (more than 2800 Au–Ag freestanding bridges, spanning a length range between 20 and 500 µm and a width range from 5 to 40 µm) were heated from 100 up to 400 °C in increments of 50 °C and then cooled down to room temperature gradually in approximately 45 min.

Between 150 and 250 °C the freestanding bridges buckled elastically without permanent deformation—the bridge returned to their original configuration when cooled to ambient. Yet it is not feasible to observe the elastic thermal buckling in the bridges during RTA. We mimicked this process on a hot plate and real-time visualized the buckling performance. Samples, both annealed by RTA and the hot plate, were determined to be flat at room temperature by the optical profiler, which indicates that the elastic buckling occurred in this temperature range. Dealloying of bridges subjected to less than 250 °C lead to cracklike failures of the vast majority of the bridges.

At 250 °C, plastic buckling of the released structures was induced, as indicated by significant permanent deformation that remained after cooling. Figure 3(a) is a scanning electron microscope (SEM) image of a sample before dealloying that was heated to 400 °C using the RTA process and then cooled to ambient. While white light interferometry measurements indicate out-of-plane deflections on the order of 1–10 µm (e.g., deflection of 13.9 µm in a 400 µm long Au–Ag bridge), after the same dealloying procedure described above, a flat profile is recovered for temperatures greater or equal to 250 °C, indicating that the residual strain induced by RTA compensates for the tensile stress developed during the dealloying step [Fig. 3(b)]. Between 250 and 400 °C, greater than 97% of the bridges are intact after dealloying, with no cracks visible in SEM images—in contrast to those exposed to lower temperatures. The high magnification SEM image in Fig. 3(c) shows a characteristic spongelike network formed when the material is dealloyed.

Based on these observations, the residual compressive strain in the bridges introduced during permanent deformation (induced by sufficient heating) clearly mitigates tensile fracture during the dealloying phase. The presence of significant plastic deformation prior to dealloying is clearly effective in reducing the likelihood of fracture. Naturally, a precise estimate of the residual strain present after heat treatment requires explicit determination of the inelastic behavior of the alloy, as well as an elastic-plastic buckling analysis that incorporates realistic inelastic material models. Although the mechanical properties of the alloy are not known explicitly, a rough estimate via the rule of mixtures implies that the modulus is ~80 GPa and the coefficient of thermal expansion is ~17 ppm/°C. This implies that the thermal strains in the range of 0.004–0.007 are induced by the temperature range of 250–400 °C, which is likely at least two to three times the yield strain of the material. While the bridges clearly undergo significant plastic deformation, at present it is difficult to identify the physical mechanisms responsible

![Fig. 2](image-url)  
**Fig. 2.** (a) Scanning electron microscope (SEM) images of a np-Au bridge ruptured after dealloying. (b) Pronounced necking is observed at np-Au ligament breakage.
for mitigating tensile failure, due to the currently unknown inelastic response of the material and the complicated stress-generation mechanisms during dealloying. This is the subject of an ongoing study that is focused on quantifying the residual stresses in freestanding bridges at all stages, including preheat treatment and pre and postdealloying.

The elastic modulus of these bridges has been characterized via beam deflection tests using atomic force microscopy (AFM). To do this, it was necessary to create np-Au cantilevered beams from the bridges created by the process described above. This was accomplished by ion milling the bridges with a Ga\textsuperscript{2+} focused ion beam (FIB). As depicted in Fig. 4, a np-Au cantilever exhibits slightly concave bending. The deflection of cantilevers is observed to be reduced significantly with low ion current, indicating that the FIB cutting and imaging introduce nonuniform thermal stresses. It is also possible that the residual stresses vary through the thickness, or the microstructure (e.g., porosity or composition) varies, or both. This is currently being examined using nanomechanical probing of intact clamped nanoporous bridges.

For the cantilever experiments used to extract the elastic modulus, an AFM cantilever with a very low spring constant (0.01 N/m) was used to obtain force-displacement curves from different locations on the np-Au cantilevers. Young’s modulus of np-Au material derived from these AFM force curves was found to be 13.4±1.7 GPa. The value of Young’s modulus measured via these beam deflection tests is consistent with that determined by nanoindenter on bulk np-Au. It should be noted that there is a close relation between Young’s modulus and nanoscale morphology of np-Au, which is under further investigation.

In summary, freestanding np-Au microbridges and cantilevers have been developed. We have demonstrated that plastic thermal buckling in Au–Ag alloy microstructures can be used to mitigate the effects of tensile strain arising from dealloying. A wide range of temperatures between 250 and 400 °C can be chosen for the rapid thermal annealing, with the key implication being that permanent plastic deformation is required to generate sufficient compressive residual strains to offset tensile stresses induced during dealloying. Finally, np-Au cantilevers created by ion milling doubly clamped bridges were characterized with AFM; these freestanding np-Au microstructures have Young’s modulus of 13.4±1.7 GPa.

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