

Microfabrication and mechanical properties of nanoporous gold at the nanoscale

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The mechanical properties of nanowires consisting of nanoporous gold are studied experimentally. The nanoporous gold is synthesized from dealloyed “white gold” leaf ($\text{Au}_{37.4}$ and $\text{Ag}_{62.6}$ in at.%) into a free-standing dog-bone-shaped specimen with a gauge section 7 μm long, 300 nm wide, and 100 nm thick. The elastic modulus, residual stress, and yield stress are measured by deflective tensile testing and nanoindentation, and are about 9 GPa, 65 MPa, and 110 MPa, respectively.

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Nanoporous metals are promising materials for a wide variety of applications [1] such as sensors, micro-actuators, fuel cells, catalysis, and microfluidic flow controllers. Several methods exist to manufacture porous or foam metals including [2], melt gas injection, gas-releasing particle decomposition, casting with polymer foams, electrodeposition, vapor deposition technique, and dealloying. During dealloying, one or more of the less noble constituents of an alloy system is dissolved from an alloy and the final product is typically composed almost entirely of the more noble alloy constituents. The resulting structure consists of an open-cellular porous material in which the connecting ligaments and the cells have dimensions of the order of tens of nanometers. The physical mechanisms of the dealloying process have been discussed in a qualitative manner [3,4]. Nanoporous gold is a particularly desirable system because of its resistance to corrosion and also the fact that the gold surface can be tailored to be sensitive to adsorption by various biological and chemical agents [5]. It can be fabricated by dealloying a gold/silver alloy in nitric acid (HNO_3).

The mechanical robustness of nanoporous systems is an important consideration in applications, yet relatively few studies have been performed to characterize the mechanical properties of nanoporous gold obtained by dealloying. Biener et al. [6,7] reported mechanical properties of nanoporous gold based on nanoindentation test, however they focused on a bulk specimen which has ligaments significantly larger than in the present study.

The goal of this study is to determine the elastic modulus, residual stress and yield stress of a nanoporous gold film. This was done by two complementary sets of measurements. The first was to measure the force and displacement response associated with deflecting a thin film of nanoporous gold suspended above a silicon substrate in a double-cantilever configuration with a nanoindenter. The second was to use a nanoindenter to probe the elastic properties and hardness of a thin film of the same nanoporous material by direct indentation while it is adhered to a silicon substrate.

Commercially available gold–silver leaf (Monarch™ 12 carat white gold– $\text{Au}_{37.4}\text{Ag}_{62.6}$ at.%, *Sepp Leaf Products, Inc.*) with an as-received thickness of about 150 nm as measured by atomic force microscopy (AFM) was employed in the study. The white gold leaf was glued onto a (001) Si wafer with epoxy in tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) solution spread uniformly by spin coating,

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followed by flattening with a smooth glass surface to obtain a final thickness of about 100 nm. The grain structure of the white gold leaf, as measured by electron backscatter diffraction (EBSD), had a strong [001] texture. An array of dog-bone shape specimens was fabricated by an electron beam lithography regimen as detailed in previous work [8]. The final step after suspending the specimens was to dealloy them in ACS grade 70% concentrated nitric acid (approximately 16 mols) for 45 min at ambient temperature. The resulting array of specimens is shown in Figure 1a and b. The gauge length of the specimen is seven micrometers and the cross-sectional dimensions of the gauge length are about 100 nm by 300 nm. The gauge length and width of the specimen were determined by the lithographic processes; the thickness of the films was measured in ten places via SEM and the average thickness was 99.8 ± 7.1 nm. Figure 1c shows the morphology of the nanoporous gold. The ligaments have a characteristic cross-section size of 20–40 nm, similar to that of other studies [1,3]. Energy dispersive X-ray (EDX) analysis confirmed that negligible silver is present. Therefore, the nanoporous Au fabricated from white gold leaf has a relative density of 35.2% as compared to that of monolithic gold.

The defective tensile tests were carried out by deflecting the center of the suspended bridge-like specimens using a nanoindenter (NanoVision™, MTS Systems Corporation, Oak Ridge, TN) with a dynamic contact module (DCM). A Berkovich indenter—a three-sided pyramid diamond tip with the same area to depth ratio as the traditional Vickers indenter—was used for this study as in [8]. To load the specimen, the nanoindenter was operated under position control (30 nm/s) to push the specimen toward the substrate until the specimen was either broken or touched the substrate. A representative micrograph of a specimen after deflection testing is in Figure 1d. It is estimated that the radius of curvature of the nanoindenter tip is approximately 150 nm, which is much larger than the ligament length.

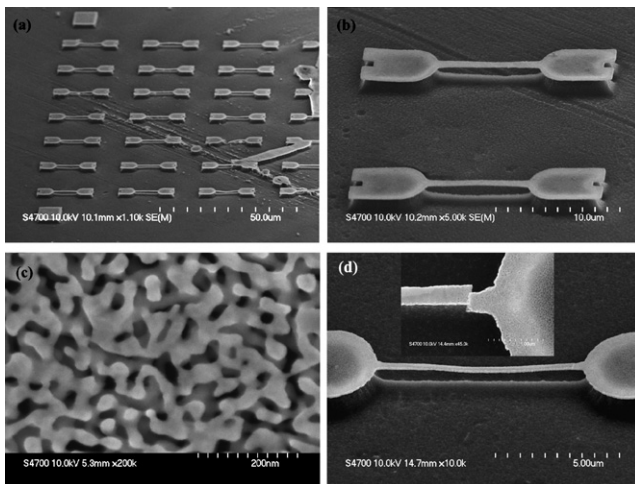


Figure 1. Micrographs of nanoporous Au bridge-like specimen for defective tensile test by nanoindenter: (a) SEM image of array; (b) an enlarged image of (a); (c) nanoporous structure and (d) specimen 2 after mechanical testing.

Load–displacement curves of three free-standing nanoporous gold specimens, 300 nm width and 100 nm thickness, are shown in Figure 2a. A sudden drop in load for each of the three specimens signals the onset of deformation localization which ultimately leads to failure across the width of the specimen. The elastic modulus of the nanoporous Au film is determined by comparing the force–displacement data to an analytical model of a center-loaded double cantilever beam for which sliding at the anchor-points is prohibited. The model which assumes a linear elastic stress–strain constitutive behavior, yet accounts for finite displacement and residual stress, is an approximate solution based upon the principle of minimum potential energy [9,10]. Accordingly, the force, F , necessary to cause an elastic vertical displacement, δ , at the center of the gauge section of the suspended film is

$$\frac{F}{Ewh} = \left(\frac{\pi^2}{2}\right) \left[\frac{\sigma_0}{E}\right] \left[\frac{h}{L}\right] \left(\frac{\delta}{h}\right) + \left(\frac{\pi^4}{6}\right) \left[\frac{h}{L}\right]^3 \left(\frac{\delta}{h}\right) + \left(\frac{\pi^4}{8}\right) \left[\frac{h}{L}\right]^3 \left(\frac{\delta}{h}\right)^3 \quad (1)$$

where L is the gauge length of specimen, w is the width of specimen, h is thickness of the film, σ_0 is the residual stress, and E is elastic modulus. The parameters E and σ_0 in Eq. (1) are fitted to the experimental data to determine values for elastic modulus and residual stress. Figure 2b shows the data and the fitted curve up to the first load drop for specimen 1. The resulting values are: Specimen 1, $E_{np} = 8.99$ GPa, $\sigma_0 = 65.0$ MPa; Specimen 2, $E_{np} = 8.33$ GPa, $\sigma_0 = 52.9$ MPa; and, Specimen 3, $E_{np} = 9.08$ GPa, $\sigma_0 = 77.7$ MPa, which gives an average of $E_{np} = 8.8$ GPa and $\sigma_0 = 65.2$ MPa, where E_{np} refers to elastic modulus of the nanoporous gold film.

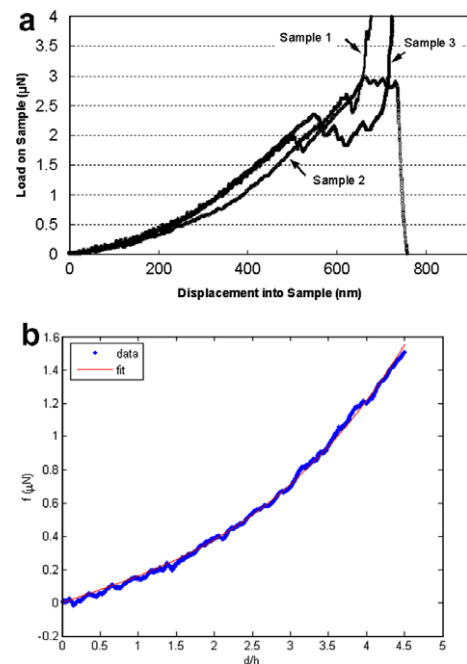


Figure 2. Experimental results: (a) load–displacement curves of free-standing nanoporous Au film deflected by nanoindenter and (b) curve fitting to non-linear beam theory.

Figure 1d shows Specimen 2 after testing. Final failure in the other two specimens occurred in the center of the gauge length at a slightly higher force than in Specimen 2.

The results of the deflection experiments can be evaluated by comparison to scaling laws. We adopt Gibson's and Ashby's analysis [11] of the physical and mechanical properties of open-cell foams to the nanoporous gold. The mass density of the nanoporous gold is expected to scale as [11]

$$\frac{\rho_{\text{np}}}{\rho_s} = C_1 \left(\frac{t}{l}\right)^2 \quad (2)$$

where ρ_{np} and ρ_s are mass density of nanoporous material and mass density of solid material, respectively, and t is ligament thickness and l is length of ligaments. C_1 is a geometric constant that is approximately unity. Average values of t and l for the nanoporous gold were determined using a standard metallographic method [12] via SEM micrographs of nanoporous gold to obtain $t \cong 32$ nm and $l \cong 53.4$ nm, which yields a relative density of 35.9%; this value agrees well with the relative density of gold in the alloy prior to dealloying, which is 35.2%.

According to Gibson and Ashby, the elastic modulus for a porous material scales as

$$\frac{E_{\text{np}}}{E_s} = C_2 \left(\frac{\rho_{\text{np}}}{\rho_s}\right)^2 \quad (3)$$

where E_s is the elastic modulus of the corresponding monolithic material, and C_2 is a constant which is approximately unity for most materials. The elastic modulus of the bulk gold, E_s is about 80 GPa [13], so the predicted elastic modulus of the nanoporous gold film, E_{np} , is in the range of 9.91–10.31 GPa depending on relative densities. This value is in good agreement with the value measured by deflection test.

The stress in the specimen which corresponds to the sudden load drop was also determined by converting the load–displacement data obtained from the deflection test to stress–strain data along the neutral axis of the specimen using the approximate solution based upon the principle of minimum potential energy [9,10]; the average value obtained for these specimens was about 190 MPa. This should be considered to be the “ultimate” stress at which the weakest set of ligaments across the section of the specimen is strained to its point of failure, while the deformation outside the region of strain localization remains elastic.

Results of the nanoindentation experiments on nanoporous gold adhered to the substrate are shown in Figure 3; the process steps to obtain the film were identical to that described in [8] except that the reactive ion etching (RIE) to suspend the films was not performed. The elastic modulus was determined using the data in Figure 3 to a depth of 20 nm using continuous stiffness measurement and standard analysis methods [14]. The average of more than 20 indentations gives an elastic modulus of $E_{\text{np}} = 13.2 \pm 3.4$ GPa, which is slightly higher than the values measured by deflection test and other studies [6,7]. This higher value could be due to the presence of the underlying substrate. This data can

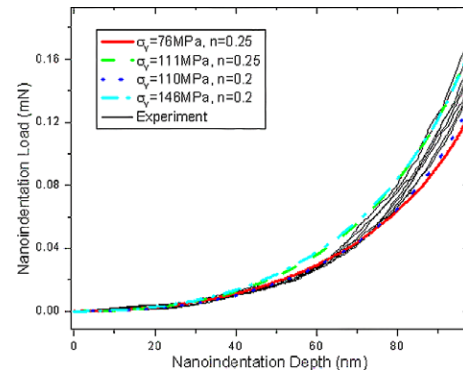


Figure 3. Nanoindentation load–depth curves measured from experiment (thin lines) vs. upper and lower bounds fitted by finite element analyses (thick lines) incorporating both substrate and densification effects.

also be used to validate the use of Eq. (1) for determination of the E_{np} and σ_0 . The maximum force at failure for the three freestanding nanoporous bridges is approximately 3 μN in Figure 2a, for which the bridge deflection was between 500 and 600 nm. Comparing this to the force and indentation depth of the nanoporous film adhered to the substrate, the depth of indentation at the load level of 3 μN is no more than 10 nm. Therefore localized crushing of the nanoporous material under the indenter is expected to be less than 10 nm in the free-standing bridge. This is on the order of 5% of the overall deformation of the bridge, which suggests that Eq. (1) is applicable.

The stress at which irreversible deformation initiates, here called the yield stress σ_y , was estimated by nanoindentation on nanoporous gold films bonded to a silicon substrate. Several nanoindentation force–displacement curves to a depth of 100 nm are shown as thin solid lines in Figure 3. The curves were analyzed using recently proposed finite element techniques [15,16], which incorporate both the substrate effect and densification effect for porous materials. The effect of substrate on the data was removed based upon a substrate effect map [16] by assuming that the substrate (Si) is much harder and stiffer than the film. Detailed finite element analyses of nanoindentation on a porous media were then carried out at fixed porosity, with film elastic modulus, residual stress, and film thickness values obtained from experiment. The plastic properties of the nanoporous gold films were varied in the simulations, including the yield stress, σ_y , and work hardening coefficient, n , which is typically about 0.2–0.25 for gold [17]. (The work hardening coefficient is defined as $\sigma = K\varepsilon^n$, where σ and ε are the uniaxial stress and strain, respectively, and K is a so-called strength coefficient. This empirical relationship is commonly used in engineering analyses and often approximately matches stress–strain data at large inelastic strains) [17]. Finally, by fitting to the upper and lower bounds of the experimental data, the yield stress of the nanoporous gold films was estimated from reverse analyses of the finite element simulations to obtain the range of $\sigma_y = 76$ –111 MPa for $n = 0.25$ and $\sigma_y = 110$ –146 MPa for $n = 0.2$ which bound the experimental results in Figure 3. The average yield stress is $\sigma_y = 111 \pm 35$ MPa.

The yield stress for a porous material is expected to scale as [11]

$$\frac{\sigma_y}{\sigma_s} = 0.23 \left(\frac{\rho_{np}}{\rho_s} \right)^{3/2} \left(1 + \left(\frac{\rho_{np}}{\rho_s} \right)^{1/2} \right) \quad (4)$$

where σ_y and σ_s are the yield stress of nanoporous gold and solid gold in the ligaments, respectively. This equation is applicable to deformation under compression and tension at the beginning stages of permanent deformation. Using the value of $\rho_{np}/\rho_s = 0.352$ and $\sigma_y = 111$ MPa leads to an estimated value of the yield stress of the individual ligaments of the nanoporous gold to be $\sigma_s = 1.45$ GPa. This implies that the yield stress of the ligaments of nanoporous gold approaches the intrinsic yield stress of gold which is on the order of 1.5–8 GPa [18–20]. Biener et al. [6] reached a similar conclusion when using a nanoindenter to test the mechanical response of bulk nanoporous gold which had a ligament size significantly larger than in the present study.

The deflection tests of the free-standing film and the nanoindentation tests of the film bonded to the substrate lead to different stress values. The nanoindentation experiments estimate the stress at which plastic, or irreversible, deformation *first* occurs to be about 111 MPa. This stress is defined as the force per unit area of the nanoporous medium, where the area includes both ligaments and cells. This value was then used to estimate the stress on the ligaments (defined as force per unit area of the ligament) at initial yield which can be as high as 1.45 GPa. Finally, the deflection test measures the stress at the *final* stages of localized deformation at the point where the plastically deforming ligaments begin to fail. This ultimate stress is defined as the force per unit area of the nanoporous medium and is on average 190 MPa for the three specimens tested. At first glance this means that the initial yield occurred at a stress of 111 MPa and that the ligaments hardened with plastic deformation up to an ultimate stress level of 190 MPa at the point of failure. According to the values of the strain hardening coefficients assumed, this would indicate that on average a 10–15% plastic strain occurred in the ligaments prior to ultimate failure. However this interpretation assumes that the localized deformation occurs uniformly across the width of the specimen, which can not be verified with current experimental setup.

In conclusion, free-standing nanoporous gold thin films were fabricated and the mechanical properties were probed both with a bridge deflection technique and also by nanoindentation. The results were analyzed in terms of non-linear beam theory and detailed finite element analysis, respectively. The results show that the elastic modulus of the nanoporous gold is about 8.8 GPa and that the initial yield stress of the nanoporous gold is about 111 MPa and that the ultimate stress at failure due to deformation localization is as high as 190 MPa.

It is then shown that the yield stress within an individual ligament may be as high as 1.45 GPa, which approaches the theoretical shear strength of the material at which adjacent atomic planes slide past one another without the mediating influence of dislocations.

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