Fabrication and Characterization of Nanoporous Gold Thin Films

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Introduction:

Nanoporous gold (NPG) thin films, less than 1 μm in thickness, have been of great interest in large part due to the fact that such materials show great promise for use in diagnostic applications [1], MEMS devices [2], or other applications that require inertness, conductivity, or increased surface area. While previous research has focused on modeling the growth of such films [3,4], there have not been many studies devoted to their mechanical properties. A knowledge of the mechanical properties of NPG films is fundamental to an understanding of issues regarding structural integrity in devices which employ such films.

The focus of this project has been to optimize the processing of NPG films on silicon substrates and to measure the induced stress in the porous gold films by the dealloying method used in the fabrication process. Changes in stress as a function of temperature were also measured. Scanning electron microscopy (SEM) was used to determine porosity changes due to exposures in various concentrations of nitric acid, and as a function of annealing. Surface-enhanced Raman (SERS) spectra of thiol self-assembled monolayers (SAMs) were acquired using a near-IR confocal Raman microscope with an excitation wavelength of 785 nm.

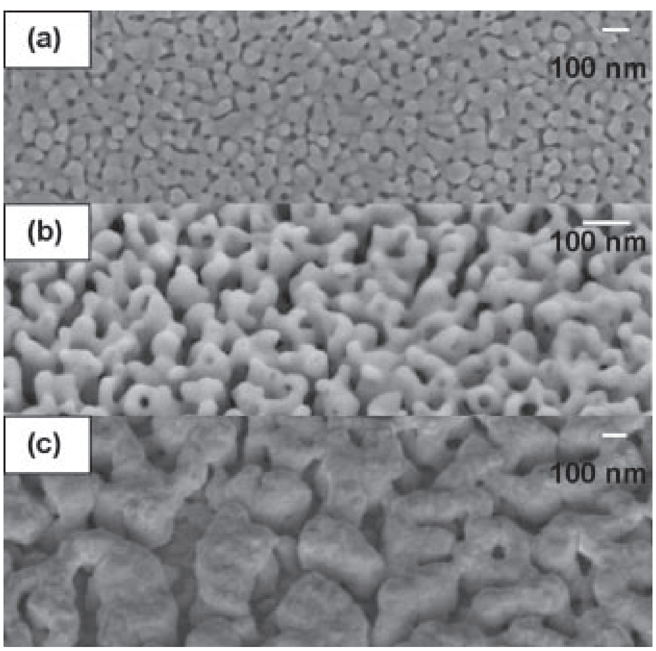

Figure 1: SEM images of nanoporous gold; (a) etched in 15% v/v HNO_3, (b) etched in 20% v/v HNO_3 (imaged at an angle), and (c) after 9 hours of annealing at 450ºC (imaged at an angle).

Fabrication:

NPG thin films (Figure 1) were prepared by selective leaching of silver from an alloy deposit consisting of $Ag_{70}Au_{30}$ [3] resulting in a mesoporous metal having pore dimensions of 10-30 nm. Three-inch Si wafers were cleaned using a standard metal-oxide semiconductor (MOS) cleaning process for 30 minutes and rinsed with ultrapure (18 MΩ-cm) water. After undergoing an additional rinse/dry cycle, the wafers were placed in a 1000°C thermal oxidation furnace for an hour to facilitate growing of 300 nm of oxide on the substrate. Upon cooling, an adhesion layer consisting of 30 nm Cr / 50 nm Au was evaporated onto the wafer, and approximately 250-300 nm of a $Ag_{70}Au_{30}$ alloy was deposited using an argon-ion sputter system. Wafers were then immersed in various concentrations of nitric acid (ranging from 15% to 40% v/v), rinsed with DI water, blown dry with nitrogen gas, and allowed to dry overnight. Substrates prepared in this manner were a dark brown in color, with increasing darkness upon immersion in higher concentrations of acid.

Results and Discussion:

Stress Analysis: Stress measurements were made using a common laser scanning technique [5], which measures substrate curvature changes associated with thin film stresses. Initially, it was believed that etching using nitric acid would result in increased stress in the porous film due to the fact that removal of silver atoms from the alloy would create a non-equilibrium level of vacancies in the vicinity of some gold atoms. In order to produce a configuration closer to equilibrium, the gold atoms would aggregate to form clusters [3]. Thus the film would become denser and pull on the Si wafer, producing a measurable change in the substrate curvature and results in an overall increase in tensile stress of the gold. However, the opposite was found to occur-the tensile stress decreased after etching. Average stress values measured in the sputtered film were around 340 MPa, which dropped to 60 MPa in the porous film after the etching process. Relaxation of stress also occurred as a result of annealing (Figure 2). Thermal diffusion of gold atoms allows atoms to relieve local stresses through rebonding.

Morphology: Pore and ligament evolution were monitored as a function of annealing at 450°C for 15 hours. Statistical analysis of pore openings using SPIP image processing software showed; (1) that the first 10 hours of annealing resulted in a near-exponential growth in the average pore width, and (2) from 10-15 hours, the average pore width appears to be closing (Figure 3). In addition, the entire process of annealing results in a linear increase in the ligament width. This evolution is also accompanied by ligament coarsening, which affects the material's ability to be used for surface-enhanced spectroscopy (see Raman discussion).

Raman: SERS is a technique that uses inelastic (Raman) scattering of monochromatic light for the detection of adsorbed molecules on roughened metal surfaces (typically gold or silver). The increase in the Raman scattering rate associated with the SERS measurement can arise either from electromagnetic or chemical enhancement effects, or both [6]. In this experiment, the vibrational modes of 1-dodecanethiol and 2-mercaptopyridine SAMs chemisorbed onto NPG substrates etched in various acid concentrations were analyzed using Raman. These molecules were chosen because of their large inherent polarizability that results in strong Raman scattering.

Enhancement for both molecules was observed on NPG substrates formed by etching in 15% and 20% v/v HNO_3 concentrations, but was not visible with increased acid concentrations (Figure 4). This observation may be due to greater quantities of residual silver in the films etched at lower acid concentrations, since silver is known to be a better SERS substrate. Such enhancement was not visible on substrates that were annealed before thiol deposition. Nanoscopic surface irregularities that are present in many SERS substrates produced by wet-chemical roughening procedures disappear upon annealing.

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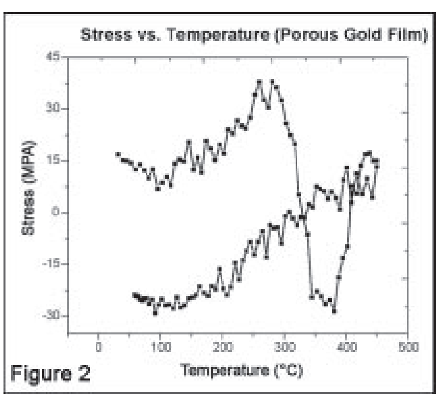

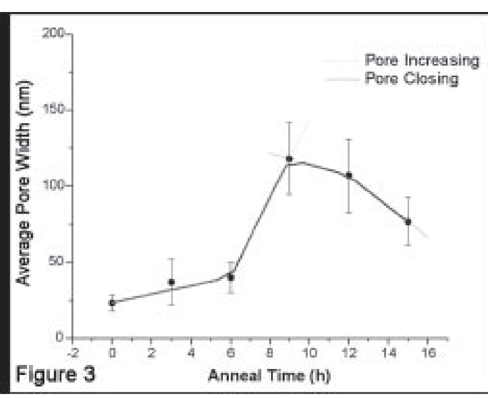

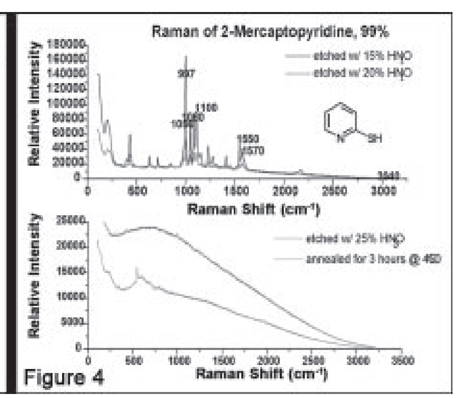

Figure 2: Stress-temperature measurement of porous gold film. A relaxation of tensile stress is occurring due to the fact that diffusion of the gold atoms allows local rebonding.

Figure 3: Porosity changes due to annealing at 450ºC for 15 hours.

Figure 4: Raman spectra of 2-Mercaptopyridine. Top: NPG substrates etched in 15% and 20% v/v HNO_3 before exposure to 1mM thiol solution. Bottom: substrates etched in 25% v/v HNO_3 or greater or subjected to annealing.