Scaling Up Catalytic Nanomotors

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Abstract:

To gain insight into the mechanism of motion of platinum/gold rods in hydrogen peroxide solution, a process was developed to fabricate micron diameter platinum/gold rods with aspect ratios similar to previously studied nanometer diameter rods. The micron diameter rods were fabricated in a sacrificial template formed using high-aspect-ratio photolithography. SJR 5740 was patterned on a silver-coated silicon wafer to form the template. The template was then connected to a standard three-electrode cell and a voltage was applied to electroplate gold, then platinum, into the template features. Once the platinum/gold rods were fabricated, the photoresist and the silver seed layer were removed, and the rods were collected and studied.

Introduction:

In previous studies done by Dr. Sen's group at the Pennsylvania State University, platinum/gold nanorods approximately 370 nm in diameter and 2 µm in length were grown electrochemically in alumina membranes. When placed in water, the rods exhibited random Brownian motion. However, when placed in a hydrogen peroxide solution, the rods catalyzed the spontaneous decomposition of hydrogen peroxide and exhibited autonomous, non-Brownian movement.

The purpose of this project was to fabricate larger platinum/gold rods with aspect ratios similar to the previous nanorods (6:1) and study their movement in hydrogen peroxide solution.

Procedure:

Fabricating the Mold: To fabricate the electroplating mold, 50 nm of silver (a conductive seed layer for electroplating) and 10 nm of chromium (an adhesion layer between the silver and silicon) were evaporated onto a silicon wafer. SJR 5740, a positive photoresist that produces high-aspect-ratio features with vertical sidewalls and resists degradation during electroplating, was dynamically spun onto the wafer at 3000 RPM for 50 seconds. The wafer was then soft-baked at 105ºC for 13 minutes. A second application of SJR 5740 was spun onto the wafer. This double coat allows for greater photoresist thickness with better uniformity than a single coat at a lower spin speed. The average thickness of the photoresist was 18-20 µm. During the coating process, the photoresist beaded along the edge of the wafer. This edge-bead was removed by applying acetone to the wafer's edge at 3000 RPM. The wafer was then soft-baked a second time at 105ºC for 13 minutes. The wafer was held at clean-room temperature and humidity for 24 hours to allow the photoresist to rehydrate before exposure. Finally, the wafer was exposed with a Karl Suss MA6 Contact Aligner at an intensity of 12 mW/cm^2 at 365 nm and developed in AZ400K diluted in DI Water (1:4). Exposure and development times were systematically varied to find the times that produced the best features [1].

The first attempt to fabricate the mold used a photolithography mask with densely packed square and rectangular features ranging in size from 1 µm to

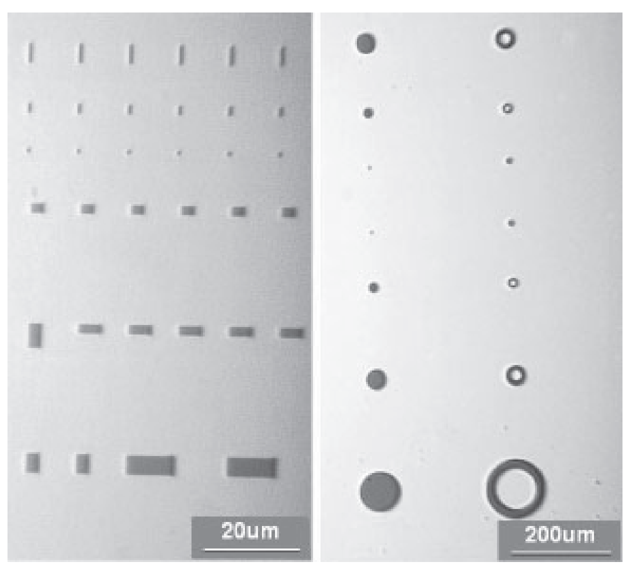

Figure 1: Photolitography masks.

50 µm (Figure 1a). Exposures with this mask produced features that did not extend down to the wafer surface. Increased exposure time created poor resolution of the smaller features, while increased development time created non-vertical sidewalls. This is believed to be due to the dense spacing of the features and the large amount of surface area being exposed.

A second attempt to fabricate the mold used a mask with loosely packed circle and ring features ranging in size from 6 µm to 60 µm (Figure 1b). With this mask, an exposure time of 150s and development time of 14m produced features with good resolution that extended down to the wafer. However, the smallest feature was 6 µm in diameter, which means with an 18 µm thick photoresist, the aspect ratio was 3:1, and not the desired 6:1. Due to time constraints, wafers with this 3:1 ratio were used to continue the work.

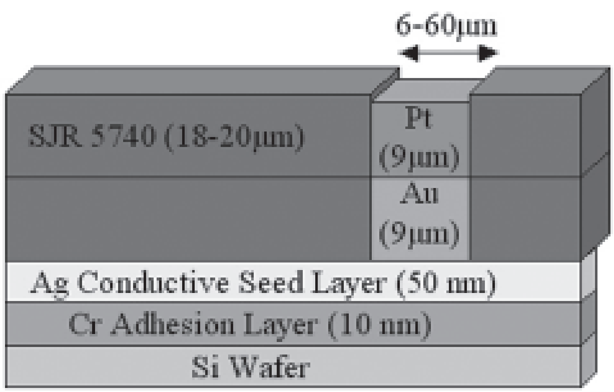

Figure 2: Overview of the fabrication process.

Fabricating the Rods: The electroplating was done in a standard three-electrode cell containing a titanium counter electrode, a silver/silver chloride reference electrode, and the electroplating mold as the working electrode. Techni Gold 25 ES, a slightly alkaline cyanide-free solution, and Techni Platinum AP, a neutral solution, were used.

Through cyclic voltammetry it was determined that the deposition potential of the gold and platinum plating solutions are -900 mV and -800 mV, respectively. The deposition rate for gold was determined to be approximately linear with a rate of 1 µm/10 min, but platinum's deposition rate was found to be non-linear.

During the platinum plating process, oxygen bubbles formed in the features of the mold. These bubbles blocked ion-transport and limited the amount of platinum that could be plated to ~ 1 µm.

Once the features had been fabricated, the silver seed layer was dissolved in 5M nitric acid leaving the rods in a photoresist "pancake". This "pancake" was removed from the nitric acid and dissolved in acetone. Finally, the rods were collected, rinsed in DI water, and ready for study in hydrogen peroxide solution.

Results and Conclusions:

The features fabricated through this process were approximately 9 µm (8 µm Au / 1 µm Pt) tall and ranged in diameter from 6-60 µm. These features did not have the desired aspect ratio and a majority of the features were discs, not rods. It was not surprising that these features did not exhibit motion (Brownian or non-Brownian) in water or hydrogen peroxide solution. Instead, the features settled to the bottom of the solution. Although rods with the desired dimensions and aspect ratio were not fabricated, a process to create a mold for electroplating micron diameter rods was successfully developed.

Further study is warranted into using this process with a different mask having loosely packed, smaller features to produce a mold that would yield rods with the desired geometry.

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References:

[1] Li, X.; Diss. UCLA, 1999.

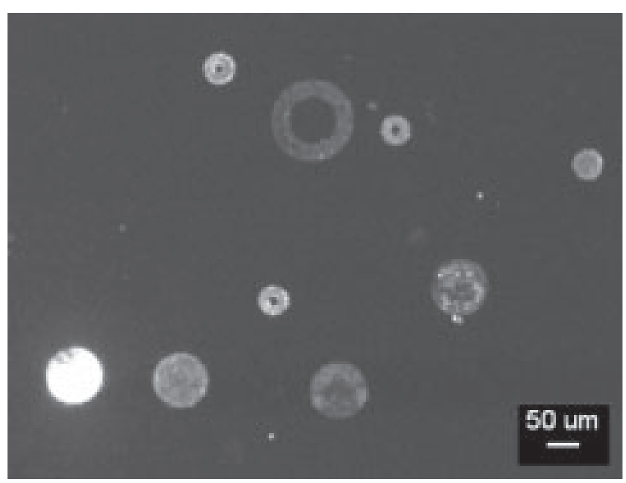

*Figure 3: Free features in DI water.
Dark field microscopy 50x.*