Patterning Silver Using an Atomic Force Microscope and Laser-induced Deposition from Liquids

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Researchers have previously investigated laser-induced deposition of metals (Au, Ag, Cu, Pd) for a variety of patterning applications.[1,2] While studying this process using a laser illuminated Atomic Force Microscope (AFM) and liquid cell, we encountered an unexpected phenomenon that could enable "negative tone" tip-based patterning. Specifically, we found that scanning an illuminated AFM tip over a substrate, locally suppresses the laser-induced deposition of silver. This effect persists for some time after scanning, and is not produced by scanning without illumination.

Experimentally, an aqueous solution containing 1mM sodium citrate ($NaC_6H_7O_7$) and 1mM silver nitrate ($AgNO_3$) was placed in an AFM liquid cell. The cell was illuminated with a focused, continuous wave laser to achieve silver photo-reduction on a glass substrate. The laser wavelength was 532nm and its intensity was varied from 1W/cm^2 to 20W/cm^2 at the substrate liquid interface. During illumination, an area of the substrate under irradiation was scanned in contact mode with a gold coated AFM tip with a radius of less than 25nm.

Silver deposition was obtained with particle sizes ranging from 50 nm to 200 nm. The scanned area presented greatly reduced deposition (Figure 1a) which one might at first attribute to simple mechanical removal of the particles by the tip. However, a second illumination of the scanned region induced little additional deposition. Further deposition in the scanned area was not observed after exchanging the solution (Figure 1b), but was observed after washing the sample and exposing it to air (Figure 1c). Exposing the sample with a projected image and subsequently flood exposing the sample did not produce the same effect (Figure 1d). Finally, patterns as small as 500 nm were resolved (Figure 2) but high resolution patterning will require smaller particle sizes and sharper tips.

In conclusion, we demonstrated a new technique to generate negative-tone silver patterns based on the suppression of photo-reduction by tip scanning during illumination. The mechanism is not fully understood, but we have ruled out purely mechanical effects, preferential deposition on previously deposited areas, and local depletion of the reactants. The persistence (at least 20 minutes) and reversibility (by exposure to atmosphere) of the process suggest an optically or thermally driven modification of the substrate surface.

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[1] G. Toth, K. Kordas, J. Vahakangas, A. Uusimaki, T. F. George, and L. Nanai, J. Phys. Chem. B **109**, 6925 (2005).
[2] K. Kordás, Applied Surface Science **172**, 178 (2001).

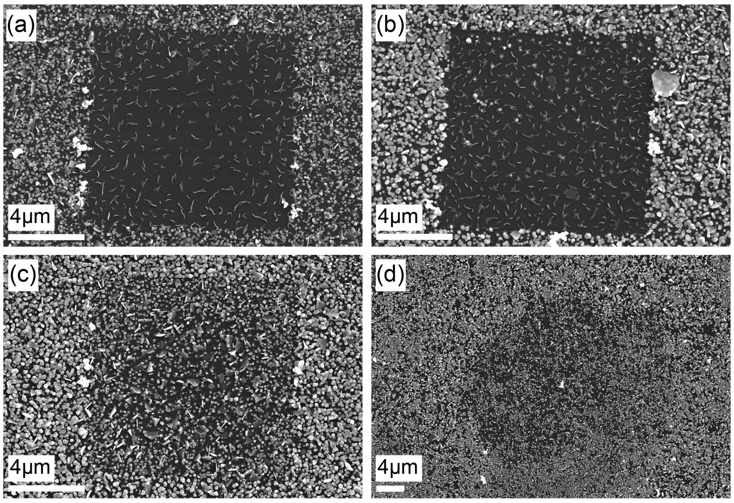

Figure 1: Laser-induced deposition of silver on a glass substrate can be locally suppressed by AFM tip scanning. (a) An area of 10 by 10 μm is scanned while the sample is illuminated for 5 minutes with an intensity of ~ 20W/cm^2. A less dense area is observed with little accumulation on the sides. (b) Another previously cleared area is illuminated, a second time, after renewing the solution without exposing the sample to air. Little to no difference is observed inside the scanned area. (c) Another area, cleared before, is now illuminated after washing the sample and renewing the solution. The scanned area is now deposited as if it was never scanned. (d) A different cleared area made with a mask is re-illuminated in order to verify that the tip scan is indeed affecting the substrate. The scale bar inside each subfigure measures 4μm.

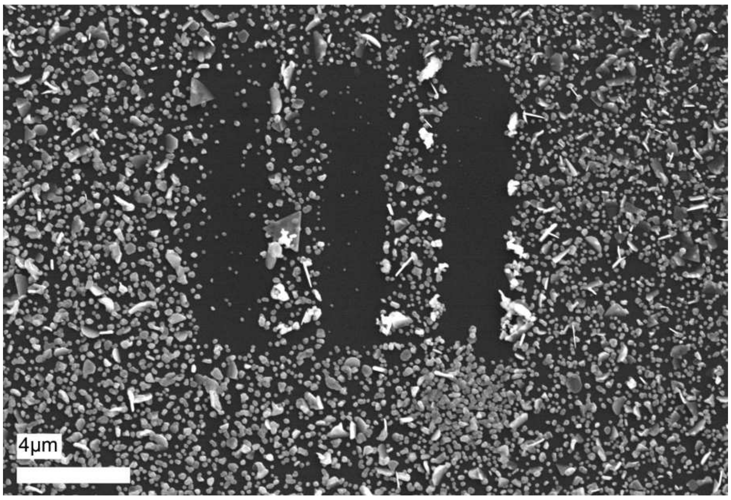

Figure 2: Laser-induced deposition of silver on a glass substrate forming bands. A pattern of three bands of 2μm width is scanned from top to bottom and left to right while the sample is illuminated for 5 minutes with an intensity of ~ 20W/cm^2. The scale bar in the figure measures 4μm.