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Citation: J. Vac. Sci. Technol. B 30, 06FD02 (2012); doi: 10.1116/1.4764093

View online: http://dx.doi.org/10.1116/1.4764093

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Silver patterning using an atomic force microscope tip and laser-induced chemical deposition from liquids

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(Received 16 July 2012; accepted 11 October 2012; published 26 October 2012)

This article presents a new direct patterning technique in which laser photoreduction of silver from a liquid is controlled by a scanning atomic force microscope tip. Contrary to expectations, the tip suppresses, rather than enhances, deposition on the underlying substrate, and this suppression persists in the absence of the tip. Experiments presented here exclude three potential mechanisms: purely mechanical material removal, depletion of the silver precursor, and preferential photoreduction on existing deposits. These results represent a first step toward direct, negative tone, tip-based patterning of functional materials. © 2012 American Vacuum Society.

I. INTRODUCTION

Techniques to form nanopatterns and nanoparticles of noble metals such as gold, silver, copper, and palladium have been developed continuously, and very diverse technologies are being used for fabrication.1–7 Some authors have analyzed the light induced formation of silver from solutions and the relationship between the size and shape of nanoparticles and the conditions of the illumination.8,9 Several groups have also formed nanopatterns by depositing noble metals on substrates by means of laser beam-triggered chemical reactions. This method is called laser-induced chemical deposition (LICD);10–12 however, a disadvantage of the patterns formed by LICD is the size, which is usually larger than 100 μm. In addition, there have been numerous applications of scanning probes, most often atomic force microscope (AFM) tips, to nanofabrication,13–16 and several of these efforts have employed laser illumination of the tip. Tseng et al.16 and Huang et al.17 used the laser beam to heat or apply a force to the tip. In this way, they elaborated patterns by indenting the sample. Lee et al.18 used an illuminated, gold coated tip to expose a photoresist and subsequently to generate gold patterns of less than 120 nm.

Here we investigate the combination of laser-induced chemical deposition with an illuminated scanning probe tip. Specifically, an aqueous solution containing a silver precursor is illuminated with a focused laser beam to photoreduce silver onto a glass substrate. While the interface of the substrate and the liquid precursor is illuminated, an AFM tip scans the illuminated area [see Fig. 1(a)]. Light incident on a sharp metallic tip generates a charge accumulation at the surface of the tip. This charge accumulation, often associated with surface plasmon polaritons and/or localized surface-plasmon resonances, is one of the causes for an enhancement in the electromagnetic field. This enhancement is higher at the apex of the tip, and hence, the field at the apex of the tip can be up to two orders of magnitude higher than the incident field.19–21 If the photoreduction due to the irradiation of the liquid precursor depends on the local electromagnetic intensity, then deposition will be accelerated in an area with a diameter approximately the radius of curvature of the tip.22 If a higher deposition rate is obtained just below the tip’s apex, the deterministic movement of the tip should generate patterns narrower than the radius of the tip.

Our experiments consistently produced the opposite effect, whereby a scan of an illuminated AFM tip over a substrate locally prevented the laser-induced deposition of silver. This effect persists for some time after scanning, which can be developed into a “negative tone” patterning technique. Thus, we demonstrate a new technique to generate negative-tone silver patterns based on the suppression of photoreduction by tip scanning during illumination.

II. EXPERIMENT SETUP

A diagram of the experimental setup and an example of the patterns that could be generated are shown in Fig. 1. An aqueous solution composed of 1 mM sodium citrate (NaCaH2O7) and 1 mM silver nitrate (AgNO3), from Sigma-Aldrich (S4641 and 209139, respectively), was introduced into an Agilent 5500 AFM using a liquid cell such that the solution was in contact with a glass slide serving as a substrate. The glass slide, from Fisher Scientific (Premium Microscope Slides Cat. No. 12-544-1), was previously cleaned by ultrasonication in acetone, isopropanol, and deionized (DI) water, for 5 min each, followed by 1 min exposure to oxygen plasma etch. The glass–liquid interface

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was illuminated with a focused, continuous wave laser in order to obtain silver photoreduction. The laser wavelength is 532 nm and was focused using a 0.25 numerical aperture objective such that its intensity ranged from 0.08 to 25 W/cm² at the substrate-precursor interface. The laser was introduced through a polarization maintaining single mode fiber to spatially filter the beam. A 15:85 beam splitter was located before the objective, and the lower intensity beam was routed to a photodetector to monitor the incident power. A section of the illuminated substrate area was scanned with the AFM probe in contact mode. The AFM probe was a Budget Sensors’ gold coated AFM tip (ContGB-G), which has a radius of curvature smaller than 25 nm.

III. RESULTS AND DISCUSSION

A. Silver deposition

The conditions to obtain photoreduction of silver from solutions containing Na-citrate and AgNO₃ have been studied extensively, and were not difficult to replicate. The deposition of silver on the glass substrate was achieved by illuminating the substrate and the solution with an intensity of approximately 20 W/cm² for 5 min. The beam waist diameter at the focal plane is about 4 μm. In order to obtain a larger deposition area (~500 μm², at least five times the size of the scanned area), the laser beam was intentionally defocused from the substrate–liquid interface. A scanning electron microscope (SEM) image (obtained using a Hitachi S4300) of the silver deposition without an AFM scanned area is shown in Fig. 2. Samples were coated with a thin layer of AuPd before imaging and analysis.

To verify the composition of the deposits, an energy dispersive x-ray spectroscopy (EDS) measurement was made on five different samples. Typical EDS data, obtained using a Hitachi S-3200 N SEM and an Evex silicon lithium detector, is shown in Fig. 3. The silver (Ag) L-family of peaks from 2.8 to 3.4 keV is only present for the deposited areas. The silicon (Si), sodium (Na), calcium (Ca), and oxygen (O) peaks are present due to the glass substrate. The peak near 3.35 keV that is present in both plots can be attributed to both silver (in the deposit) and potassium (in the substrate). No precursor residue is expected to remain on the substrate since the precursor salts (AgNO₃ and Na-citrate) are highly soluble in water and the deposited sample was washed thoroughly. Furthermore, none of the SEM images showed any structure that would be typical of the crystallized salts. This indicates that the particles are primarily silver with little or no residual precursor. Washing in flowing deionized water and drying in flowing air were conducted without any special precautions, and no obvious adhesion problems were observed.

AFM measurements returned particle height from 50 nm at the edge of the deposited area to 200 nm in the denser section of the deposition (the area with maximum intensity of illumination). Areas of 10 μm by 10 μm were scanned in tapping mode with a resolution of 512 lines at a speed of 0.71 lines per second. Fig. 4 shows an AFM three dimensional view of a densely deposited area. A roughness analysis from this data obtained with Gwyddion software returned an $S_a$ (arithmetic average of the surface) equal to 21.6 nm and an $S_q$ (RMS average) equal to 30.2 nm, respectively.

B. Illumination of a scanning tip

Once the system was proven to form a consistent deposition, the tip was brought into the illuminated area. As mentioned above, electromagnetic principles suggest an intensity enhancement at the apex of the tip. This enhanced electromagnetic field was expected to generate greater deposition...
suppression of deposition observed in the experiments. Specifically, a purely mechanical cause does not explain why the deposition is uniform. One would expect that flushing the tip and particles during illumination reduces the adhesion of the particles to the substrate.

There are several possible explanations for this lack of enhanced deposition near the tip but the most probable comes from using contact mode for the scan. In contact mode, the tip is touching the surface of the sample at all times. In this way, the lateral force the tip applied to the newly formed particles is sufficient to detach them from the substrate and push them to the sides of the scanned area and/or suspend them in the solution. Several investigations have been made by different authors to show that manipulation of nanoparticles is easily achieved with a moving AFM tip.28,29

A second explanation comes from setting up the laser illumination practically at a 0° angle with respect to the substrate normal. As several authors have reported previously, a greater field enhancement is obtained for the electric field component that is along the tip axis (i.e., normal to the substrate).19,30 In our experiment, only a small component in this direction is present, due to the focusing of the laser beam, leading to reduced field enhancement.

Mechanical particle removal might explain the lack of enhanced deposition; however, it does not explain the suppression of deposition observed in the experiments. Specifically, a purely mechanical cause does not explain why the suppression of deposition is uniform. One would expect that regions scanned earlier in the process, e.g., the top of the cleared region in Fig. 5, would refill with material while the remainder of the scan is being executed. Such refilling does not occur, even during scans that require far more time than the deposition process, and a more complex mechanism must be sought to explain the phenomenon.

Thus, we conducted a series of experiments to elucidate the suppression mechanism. First, we show that suppression of deposition persists for at least 10 min, even during subsequent laser exposure in the absence of a scanning tip. This suggests either a tip-induced surface modification or a preferential deposition on previously deposited particles. However, we rule out a purely tip-based modification by showing that prescanning the surface before illumination, rather than during illumination, has little effect. We also show, using an optical projection approach, that preferential deposition on previously deposited material does not explain the phenomenon. Thus, the substrate surface is modified only by simultaneous illumination, scanning, and perhaps partial deposition. In support of this, we show that the suppression of deposition is reversible by exposing the substrate to the atmosphere, but not to fresh precursor solution. Ultimately, this series of experiments narrow down the cause of suppressed deposition to a persistent, but reversible, surface modification.

C. Evaluation of the conditions for the suppression of deposition

To verify if the force in contact mode is sufficient to remove particles from the substrate we illuminated a sample and scanned it after obtaining deposited particles. Although the tip is able to move particles, only some of the particles were removed. This is not surprising because the lateral force applied to the particles by the tip after deposition is likely far smaller than when scanning during illumination. This can be an entirely mechanical effect. The tip will not be in full lateral contact with the particles because the film-like characteristic of the deposit does not allow the penetration of the tip (see Fig. 4). Or it could be that illumination and heating of the tip and particles during illumination reduces the adhesion of the particles to the substrate.
Note that, in Fig. 5, the size of the cleared area is very similar to the size of the area scanned (10 μm by 10 μm). However, another experiment showed that a laser illumination for just 2 min leaves a considerable amount of particles deposited in the sample. The top region of the cleared area shows a much smaller quantity of particles. This region has been exposed to illumination of at least 4 min after the tip scanned it; however, the deposition is far less than we would expect from a 4 min illumination. This detail prompted us to study the behavior of scanned regions and determine if the scanning is indeed removing the deposited particles and preventing future deposition in the scanned area.

We first confirmed that scanning during illumination suppressed deposition for some time after the tip is removed. A convenient experiment to confirm this is to scan an area during illumination for 5 min; after the scan is finished, another illumination of 5 min takes place over the same area without scanning. As shown in Fig. 6, after a complete second illumination of 5 min without a second scan, the deposition of silver nanoparticles inside the previously scanned area was very limited. This indicates that either the scanning tip prevents deposition by modifying the surface, or that any subsequent deposition occurs preferentially on the particles deposited during the first illumination.

To determine whether the tip alone modifies the surface, an experiment was conducted in which the surface of the substrate was scanned before any illumination. Afterwards the same area was illuminated in the absence of the tip. In this case, the scanned area was redeposited with silver, and the deposit appeared more or less the same as the surrounding area. In three out of four experiments, the deposition was so uniform that it was not possible to identify in the SEM images any difference in the deposition between the area scanned and the other nonscanned areas. In one of the pictures, a difference in particle density was observed; however, the density difference was not as clear as it was seen in Fig. 5 for the first experiments in which the scan was made during the illumination. This indicates that suppressed deposition only occurs when the area is scanned and illuminated simultaneously.

Another possible explanation for the lack of deposition in a subsequent illumination is that the metallic silver created in the second illumination could be deposited on top of previously deposited particles more easily than on top of a cleared substrate. To test this, an illumination was made using the projected image of a mask to form a clean area [see Fig. 7(a)] as a control. Next, another clean area was made with the same mask, and then, a second uniform illumination was done to determine if there was any deposition suppression in the nondeposited area. The formerly clear area was deposited without any suppression [see Fig. 7(b)], indicating that a scan with an illuminated tip is essential in order to suppress deposition.

Two additional experiments were performed in order to observe the reversibility of the suppression of deposition. In both of these experiments, the first step was to do an initial illumination while the tip scanned the area for 5 min, thus creating a deposited spot with a cleared 10 μm by 10 μm area. After this initial scan during illumination, the two experiments differ. In the first experiment, the liquid precursor was replaced without exposing the sample to the atmosphere; in the second experiment, the sample was washed with DI water and dried by means of flowing air. Next, a second illumination with a similar intensity, than the one used.

Fig. 6. Silver deposition on glass substrate formed after two illuminations, the first one during scanning. The sample is illuminated two times: while a 10 μm by 10 μm area is scanned at a speed of 16.7 μm/s, and without the scanning tip. As expected, the quantity of particles inside and outside of the scanned area is greater compared to the image in Fig. 5 where there is no second illumination. The number of particles inside the scanned area, however, is much lower than would be expected in a first illumination without scanning experiment.

Fig. 7. Comparison of redeposition using a mask instead of a scanning tip for preventing deposition. (a) SEM image of the deposition of silver with clean areas generated using a mask to block the laser illumination. (b) SEM image of the results of a double illumination. The first illumination is made using a mask and the second illumination is made without the mask. It is shown in (b) that the second illumination (without the mask) induces deposition in every region, regardless of whether the region is already covered in deposits or not.
for the first illumination, was performed for each sample but without a scanning tip.

For the first experiment, the results were very similar to the ones obtained when a second illumination was performed without changing the solution (cf. Fig. 6). This result ruled out a simple depletion of silver or citrate ions near the deposit in the static solution. This was not surprising given that diffusion alone should be sufficiently fast to replenish the region on a time scale far shorter than the duration of these experiments.

The second experimental results are shown in Fig. 8. The second illumination (without scanning) generated new deposits even inside the previously cleared area. The SEM image in Fig. 8 can be compared with that shown in Fig. 6. Both experiments are exposed to a second dose of illumination after a scan-during-illumination procedure; however, the deposition inside the scanned area seen in Fig. 8 is much greater than the one seen in Fig. 6. It can be observed that the number and size of the particles inside the scanned area deposited after washing the sample are similar to the particles surrounding the scanned area in Fig. 5. This is clear evidence that exposure to the atmosphere returned the sample’s surface to the original state. Any illumination after the sample washing will generate the same rate of growth in the previously scanned area as if the area had never been processed.

D. Patterning

We have shown that the growth reduction at the second illumination is due to the contact of the sample with the illuminated tip. Also, the experiment in which the surface characteristics are reset shows that the mechanism of growth is much more complicated than initially expected. Nonetheless, negative-tone patterns can be made using this technique. Figure 9 demonstrates the feasibility of generating patterns smaller than 10 μm by 10 μm squares.

To form a useful pattern, the tip should move in a deterministic manner during illumination. To that end, the PicoLith tool, included in Agilent’s PicoView 1.8.2 software, is used to develop simple patterns by controlling the piezoelectric device that moves the AFM tip. A pattern can be generated by illuminating an area of the substrate and scanning the regions where it is not desired to have silver. These patterns will persist even during subsequent illumination as long as the sample is not washed. To verify the patterning technique and understand its quality and limitations, several simple patterns were made. The most promising results were obtained when patterning a series of bands of width equal to 2, 1, and 0.5 μm, separated by a distance equal to the width of the scanned bands. Figure 9 shows the SEM image of the case where five vertical bands of 1 μm in width were scanned. Each of the scanned bands was separated from the other by 1 μm. Aside from the large gaps of regions without silver, which can be optimized by varying the dose of illumination, the patterns formed by the scanning bands of 2 μm and 1 μm width were generated correctly. The width of the cleared sections was not exactly 2 and 1 μm, and the cleared sections are wider than the deposited sections. The patterns generated with the 0.5 μm wide bands presented high irregularities: sections without deposits, and large particles in the regions that were supposed to be cleared. Most of the particles present in these experiments are relatively large (see Fig. 9). The large size of the particles, some of which are at least 250 nm in diameter, limits the generation of narrower patterns because the tip drags these large particles and they bump into other particles to form large clusters. These clusters move to cleared areas and generate large gaps in the deposited areas. The deposition method is currently limited with respect to density of the deposited areas and size of the particles; however, we expect that these obstacles can be overcome with a detailed study of illumination dose and solution chemistry.

IV. CONCLUSION

In summary, enhanced photodeposition near a metallic scanning probe tip was not observed for the narrow range of conditions considered here. Mechanical displacement of the particles by the tip may counteract the enhanced deposition;
however, the illumination conditions were also not favorable to produce a large field enhancement. For future efforts the angle of incidence should be tuned to obtain maximum field enhancement, and the tip should not be in contact with the sample to prevent particle movement. The most important effect observed in this study was the suppression of deposition after scanning with the tip during illumination. Neither scanning with the tip in the absence of illumination nor pre-depositing material reproduces the effect. The clearing effect lasts at least 10 min while the sample remains covered by a liquid; however, after the sample is washed and dried, silver can be deposited again with the same rate. One speculative explanation for these results is that when deposited particles are removed by the scanning tip, the defect, impurity, or contaminant that served as a nucleation site is also removed. If so, the experiments also suggest that the nucleation sites can be reintroduced by exposure to atmosphere. Regardless, the three simplest mechanisms for deposition suppression have been ruled out and a solid foundation for future work has been established.

The effects described above can form the basis for a method for negative tone, tip-based patterning. However, more refinement is required to produce truly nanoscale patterns. Developing photoinduced deposition processes that produce denser films containing smaller particles and alternative materials will be an important first step. If successfully extended, the technique could provide a new approach to nanoscale rapid prototyping and semiconductor mask repair. Regardless, suppression of photoinduced deposition by a scanning probe can be counted among a small group of nanopatterning approaches that directly deposit functional materials in a single step.

ACKNOWLEDGMENTS

The authors thank Greg Schardein for taking the EDS spectra and Gazi M. Huda for his valuable comments and suggestions. Experiments described here were conducted in part in the Center for Nanoscale Science and Engineering (infrastructure established under NSF Grant No. EPS-0447479) and Electron Microscopy Center at the University of Kentucky. This work was supported by the National Science Foundation under Grant No. CMMI-0800658.

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