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Sacrificial nanoparticles to remove the effects of shot-noise in contact holes fabricated by E-beam lithography.

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Abstract:	Nanopatterns fabricated with extreme ultraviolet (EUV) or electron-beam (E-beam) lithography exhibit unexpected variations in size. This variation has been attributed to statistical fluctuations in the number of photons/electrons arriving at a given nanoregion arising from shot-noise (SN). The SN varies inversely as the square root of a number of photons/electrons. For a fixed dosage, the SN is larger in EUV and E-beam lithographies than for traditional (193 nm) optical lithography. Bottom-up and top-down patterning approaches are combined to minimize the effects shot noise in nano-hole patterning. Specifically, an amino-silane surfactant self-assembles on a silicon wafer that is subsequently spin-coated with a 100-nm film of a PMMA based E-beam photoresist. Exposure to the E-beam and development uncovers the underlying surfactant film at the bottom of the holes. Dipping the wafer in a suspension of negatively charged, citrate-capped, 20-nm gold nanoparticles (GNP) deposits one particle per hole. The exposed positively-charged surfactant film in the hole electrostatically funnels the negatively charged nanoparticle to the center of an exposed hole, which permanently fixes the positional registry. Next, by heating near the glass-transition temperature of the photoresist polymer, the photoresist film reflows and engulfs the nanoparticles. This process erases the holes affected by SN but leaves the deposited GNPs locked in place by strong electrostatic binding. Treatment with oxygen plasma exposes the GNPs by etching a thin layer of the photoresist. Wet-etching the exposed GNPs with a solution of I2/KI yields uniform-sized holes located at the center of indentations patterned by E-beam lithography. Experiments presented show that the approach reduces the variation in the size of the holes caused by SN from 35 % to below 10 %. The method extends the patterning limits of transistor contact holes to below 20 nm.
Author Comments:	As mentioned in the telephonic conversation with Benjamnin Werth, I would like the

	video production to be put on hold until I confirm that I have funding. At the momment I have raised roughly half the cost.
Additional Information:	
Question	**Response**
If this article needs to be "in-press" by a certain date, please indicate the date below and explain in your cover letter.	

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Benjamin Werth
Associate Editor for Chemistry at JoVE
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Dear Benjamin,

I am pleased to present an updated version of our article entitled "Sacrificial nanoparticles to remove the effects of shot noise in contact holes fabricated by E-beam lithography," by Moshood K. Morakinyo and I, for publication consideration in JoVE.

In this work, we exploit recent rapid advances in the synthesis and isolation of monodisperse nanostructures, as templates to develop sub 20nm electrical contacts for transistor source and drain. As the size of the transistor gate continues to shrink the corresponding source and drain contacts must shrink proportionately. At the current level of technology, approaching 14nm gate lengths, new effects emerge and degrade the overall yield of fabrication. Chief amongst them are the line-edge roughness (LER) and size fluctuation arising from the statistical fluctuations in number of photons/reactive molecules in a given nanoregion (the so-called shot noise(SN) effect).

The science behind the method is based on the electrostatic funneling to direct charged nanostructures to the center of the patterns in photoresist polymer thin films. Once anchored, the nanostructures provide a template that could reshape pattern in the resist film using surface tension effect. Specifically the method integrates top-down and bottom-up processing steps involving: (a) rough lithographic patterning, (b) size/shape selected nanostructure deposition, (c) resist reflow around the nanostructures, and (d) selective removal/etching of the nanostructures.

The significance of the work includes the following.

(1) It is compatible with the standard VLSI processing and hence potentially adaptable in high volume manufacturing.

(2) Any reflowable resist can be used for this type of patterning.

(3) Effects of shot noise (observed in optical, e-beam, X-ray, EUV lithography) and line edge roughness (SN/LER) are removed using size-controlled nanostructures.

(4) One specific application of the method discussed in the letter describes patterning vias for transistor source and drain contacts using nanoparticles.

(5) Wide range of nanomaterials based on metals, insulators and semiconductors can be used as long as they can be selectively etched.

As this work is interdisciplinary, I have suggested reviewers well versed in both technological and scientific aspects of this type of applied research including, a physicist, an electrical engineer and a chemist.

The work was conducted at the Portland State University supported by Intel Corporation. The e-beam fabrication was performed at the CAMCOR user facility located at the University of Oregon which was supported by ONAMI (Oregon Nanoscience And Microtechnolgy Institute) . Portland State University has filed a patent based on this work; however, neither I or my student has any financial conflict of interest with respect to this work. Please let me know if you need any additional information. Best regards,

7/1/2016

X 

Shankar B. Rananavare
Research Associate Professor
Signed by: Shankar Balalasaheb Rananavare

TITLE:
Use of sacrificial nanoparticles to remove the effects of shot-noise in contact holes fabricated by E-beam lithography.

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KEYWORDS:
E-beam/EUV lithography, electrostatic funneling, resist reflow, plasma etching

SHORT ABSTRACT:
Uniformly sized nanoparticles can remove fluctuations in contact hole dimensions patterned in poly(methyl methacrylate) (PMMA) photoresist films by electron beam (E-beam) lithography. The process involves electrostatic funneling to center and deposit nanoparticles in contact holes, followed by photoresist reflow and plasma- and wet-etching steps.

LONG ABSTRACT:
Nano-patterns fabricated with extreme ultraviolet (EUV) or electron-beam (E-beam) lithography exhibit unexpected variations in size. This variation has been attributed to statistical fluctuations in the number of photons/electrons arriving at a given nano-region arising from shot-noise (SN). The SN varies inversely to the square root of a number of photons/electrons. For a fixed dosage, the SN is larger in EUV and E-beam lithographies than for traditional (193-nm) optical lithography. Bottom-up and top-down patterning approaches are combined to minimize the effects of shot noise in nano-hole patterning. Specifically, an amino-silane surfactant self-assembles on a silicon wafer that is subsequently spin-coated with a 100-nm film of a PMMA-based E-beam photoresist. Exposure to the E-beam and the subsequent development uncover the underlying surfactant film at the bottoms of the holes. Dipping the wafer in a suspension of negatively charged, citrate-capped, 20-nm gold nanoparticles (GNP) deposits one particle per hole. The exposed positively charged surfactant film in the hole electrostatically funnels the negatively charged nanoparticle to the center of an exposed hole, which permanently fixes the positional registry. Next, by heating near the glass transition

temperature of the photoresist polymer, the photoresist film reflows and engulfs the nanoparticles. This process erases the holes affected by SN but leaves the deposited GNPs locked in place by strong electrostatic binding. Treatment with oxygen plasma exposes the GNPs by etching a thin layer of the photoresist. Wet-etching the exposed GNPs with a solution of I_2/KI yields uniform holes located at the center of indentations patterned by E-beam lithography. The experiments presented show that the approach reduces the variation in the size of the holes caused by SN from 35% to below 10%. The method extends the patterning limits of transistor contact holes to below 20 nm.

INTRODUCTION:

The exponential growth in computational power, as quantified by Moore's law[1,2] (1), is a result of progressive advances in optical lithography. In this top-down patterning technique, the achievable resolution, *R*, is given by the well-known Raleigh theorem[3]:

$$R \propto \frac{\lambda}{NA}$$

Here, λ and *NA* are the light wavelength and numerical aperture, respectively. Note that $NA = \eta \cdot Sin\vartheta$, where η is the refractive index of the medium between the lens and the wafer; $\vartheta = tan^{-1}(d/2l)$ for the diameter, *d*, of the lens, and the distance, *l*, between the center of the lens and the wafer. Over the last fifty years, the lithographic resolution has improved through the use of (a) light sources, including excimer lasers, with progressively smaller UV wavelengths; (b) clever optical designs employing phase-shift masks[4]; and (c) higher *NA*. For exposure in air ($\eta = 1$), *NA* is always less than unity, but by introducing a liquid with $\eta > 1$, such as water[5], between the lens and the wafer, *NA* can be elevated above *1*, thereby improving the resolution of immersion lithography. Currently viable paths to a 20-nm node and beyond include extreme UV sources ($\lambda = 13$ *nm*) or patterning techniques using complex double and quadruple processing of a multilayered photoresist[6,7].

At nanometer-length scales, statistical fluctuations, caused by shot-noise (SN), in the number of photons arriving within a nano-region cause variation in the dimensions of lithographic patterns. These effects are more pronounced with exposure to high-energy EUV light and E-beams, systems that need orders of magnitude fewer photons/particles compared to normal optical lithography[8]. Supersensitive chemically amplified (with a quantum efficiency > 1) photoresists also introduce a chemical SN caused by a variation in the number of photoreactive molecules in exposed nanoregions[9,10]. Lower sensitivity photoresists that need longer exposures suppress these effects, but they also reduce throughput.

On the molecular scale, the contribution to line-edge roughness from the molecular size distribution inherent to the photoresist polymers may be reduced by using molecular resists[11]. An approach that is complementary to this top-down processing of nano-patterning is the use of bottom-up methods[12,13] that rely specifically on the directed self-assembly (DSA) of diblock polymers[14]. The ability of these processes to direct nucleation and to create non-uniform spacing between desired patterns, such as holes or lines, remains challenging. The size

distribution of molecular components[15,16] also limits the scale and yield of fabrication[17,18]. Similar problems limit microcontact printing of nanoparticles in soft lithography[19].

This paper presents studies of a new hybrid approach (Figure 1; Insert Figure 1 here) that combines the classic top-down projection lithography with electrostatically directed self-assembly to reduce the effect of SN/line-edge roughness(LER)[20]. Positively charged amine groups on self-assembled monolayers (SAMs) of N-(2-Aminoethyl)-11-amino-undecyl-methoxy-silane (AATMS) underlying the PMMA film are exposed after development. The negatively charged photoresist film of PMMA electrostatically funnels negatively charged gold nanoparticles (GNPs), capped with citrate,[21-24] into SN-affected holes[25]. Re-flow of the PMMA photoresist engulfs predeposited nanoparticles in the film.

The electrostatic interaction between the oppositely charged GNPs and amine groups on the substrate prevents the displacement of the GNPs from the binding site. The reflow step maintains the relative location of the GNPs but erases the holes and the effects of SN/LER. Plasma/wet etching steps regenerate holes that have the size of the GNP. Reactive-ion etching transfers their pattern to SiO_2 hard-mask layers[26]. The method relies on using more uniformly sized nanoparticles than a patterned nanohole (NH), expressed as the standard deviation, σ, such that $\sigma_{GNP} < \sigma_{NH}$. This report focuses on steps (4 & 5 described in Figure 1) involving the deposition of nanoparticles from dispersion and the reflow of the photoresist around them to assess the advantages and limitations of the method. Both steps are, in principle, scalable to larger substrates, requiring no extensive modification of the current flow of producing modern integrated circuits on chips.

PROTOCOL:

1. Derivatize and Characterize the Surface of the Silicon Wafers.

1.1 Clean the surface of wafers using Radio Corporation of America (RCA) cleaning solutions SC1 and SC2.

1.2 Prepare SC1 and SC2 by volumetrically mixing the following chemicals:
SC1: H_2O_2:NH_4OH:H_2O = 1:1:5 v/v and SC2: H_2O_2:HCl:H_2O = 1:1:5 v/v.

1.2.1 Immerse the wafer in SC1 for 10 min at 70 °C, and then perform a deionized water wash.

1.2.2 Follow a similar protocol for SC2 (10 min at 70 °C, followed by a wash).
NOTE: The cleaning procedure removes organic and ionic impurities and generates silanol groups on the silicon oxide surface of the silicon wafers.

1.3 Derivatize the surfaces of the silicon wafers with AATMS

1.3.1 Incubate the cleaned silicon wafer in 0.05 M AATMS (prepared in dry toluene) at 80 °C for 20 min. Sonicate for 5 min in a 100-W sonicator at room temperature in pure toluene for 5 min and dry in a stream of nitrogen gas.

1.4 Characterize the surfaces of the derivatized silicon wafers

1.4.1 Measure the contact angle using a goniometer and ImageJ software[25].

1.4.2 Determine the thickness of the films using an ellipsometer (He-Ne laser light source, λ = 632.8 nm, fixed incidence angle of 70°)[25].

1.4.3 Estimate the surface elemental composition by X-ray photoelectron spectroscopy (XPS)[25].

2. E-beam Patterning.

2.1 Spin-coat photoresist (2% poly(methyl methacrylate (PMMA) in anisole) on AATMS-derivatized wafers at 4,000 rpm for 60 s.

2.2 Prebake the film at 180 °C for 120 s to dry the photoresist film.

2.3 Measure the photoresist film thickness using an ellipsometer. Ensure that the He-Ne laser light source, λ = 632.8 nm, is fixed at an incidence angle of 70°. Optimize the sample stage to maximize the detector signal using a reflective surface such as silicon wafer. Use the ellipsometer measurement program (GEMP) on the attached PC to measure the photoresist film thickness; it should be about 100 nm.

2.4 E-beam exposure:

2.4.1 Transfer the wafer to a high-vacuum chamber of an E-beam aligner.

2.4.2 Create a poker dot hole pattern using an electron beam (30 KV accelerating voltage, 37 pA beam current) passing through a 10-µm aperture and providing a 24 $\mu C/cm^3$ dosage.

2.4.3 Adjust the pattern pitch and dosage as needed to produce a poker dot-type hole-pattern of the desired hole diameter (80 nm) and pitch (200 nm).

2.4.4 Remove the wafer from the E-beam chamber.

2.5 Develop the lithographic pattern:

2.5.1 Begin pattern development in a solution of methylisobutyl ketone/isopropyl alcohol (MIBK/IPA, 1:3 (v:v)) for 70 s.

2.5.2 Continue to develop further by immersion in IPA for 30 s. Complete the development by washing in deionized water for 30 s. Dry the wafer in a stream of nitrogen gas.

3. Deposition of GNPs into E-beam-Patterned Holes.

NOTE: Deposition of GNPs in patterned holes employs two different methods.

3.1 Immerse pre-patterned wafers in GNP solutions (Method 1).

3.1.1 Leave the sample in the GNP suspension medium for 24-48 h, depending on the size of the GNP and the diameters of the holes. Use a 20-nm, citrate-capped GNP suspension containing 7.0 x 10^{11} NPs/mL.
NOTE: One may employ a GNP size from 10-100 nm and a concentration range from 5.7x10^{12}-5.7x10^{9} NPs/mL, as provided by Ted Pella. Note that the deposition density obeys the diffusion law ~$(Dt)^{1/2}$, where D and t are diffusion coefficients of the nanoparticle and deposition time, respectively (*i.e.,* smaller particles take a shorter time for deposition, as discussed in reference 20, Figure 2c).

3.2 Spray-deposit GNPs on the patterned wafers (Method 2)

3.2.1 To deposit GNPs by evaporation, spray a solution of GNPs onto the patterned substrate, placed horizontally. Orient the hand-held sprayer (Method 2) so that the spray is directed perpendicularly to the substrate surface.

3.2.2 Spray a sufficient volume of the suspension solution to wet the entire substrate surface.
NOTE: It may be necessary to dilute the GNP suspension by 10X to avoid forcing multiple nanoparticles into a large hole.

3.2.3 Incubate samples on a hot plate maintained at 30-35 °C to produce controlled evaporation for 10 min.

3.3 After deposition (by either Method 1 or Method 2), mildly ultrasonicate (100 W) the samples in deionized water for 50 s and dry in a stream of nitrogen gas.

4. Scanning Electron Microscopy Imaging.

NOTE: Two types of studies involved conventional top-down and cross-sectional SEM imaging.

4.1 For top-down SEM images, use an E-beam accelerating voltage of 5 kV at a current of ~300 µA to prevent damage to the photoresist film.
Caution: The lowest possible voltage and current setting are necessary to reduce chain scission reactions in the photoresist. These chain scission reactions reduce the glass transition temperature of the polymer, which in turn affects the operational temperature for the resist reflow step described below.

4.2 Cross-section imaging:

4.2.1 Sputter-coat 10 nm of thick gold film over PMMA photoresist to prevent ion-beam damage. Use a focused Ga ion beam operated at 30 kV and 93 pA to cut through the holes. Obtain cross-section SEM images by tilting the wafer from its normal horizontal position.

5. Reflow of PMMA Photoresist around GNPs in the Patterned Holes.

5.1 Heat the patterned substrates on a hot plate at T_{reflow} (100 °C) for 3 min, which is below the pre-determined glass transition temperature, T_g (110 °C), of 950,000 g/mol PMMA; the rate of reflow for the polymer was 1.7 ± 0.1 nm/s.

Caution: Significantly faster reflow occurred for the patterned areas that had previously been exposed to the E-beam during imaging with scanning electron microscopy (SEM), perhaps because of the cleavage of the polymeric backbone chain during exposure to the electron beam, leading to a reduction of T_g. This observation is supported by the studies from Keymeulen and co-workers, who noted that exposure to X-ray radiation reduced the T_g of PMMA[27].

6. Dry- and Wet-Etch.

6.1 Dry-etch for sufficient duration (55 s) with oxygen-plasma to expose GNPs covered with a thin film of PMMA after reflow. Carefully monitor the rate of PMMA film etching as a function of time using an ellipsometer or thin film thickness monitor.

NOTE: A too-short etching duration may not expose the GNPs, while etching for too long would completely remove the PMMA film. For 950 kD PMMA, the etch rate was 1.5 nm/s, necessitating 55 s of etching time.

6.2 Wet-etch GNPs at the bottom of the contact holes after reflow using a solution of iodine, containing 1.0 g of iodine crystal (I_2), 4.0 g of potassium iodide (KI), and 40 mL of deionized water, for 10 min.

NOTE: Potassium iodide improves the solubility of the iodine in solution and facilitates gold etching. The reaction of gold with iodine ($2Au + I_2 \rightarrow 2\ AuI$) produces gold iodide, which is slightly soluble in aqueous solution at room temperature.

7. Calculation of Particle Displacement, Density, and Fill Fraction.

7.1 Locating the hole center and GNP displacement:

7.1.1 By hand, draw horizontal and vertical best-fit straight lines through the rows and columns of holes, respectively, to established hole centers at the intersections of these lines (Figure 2a and b). Include at least 500+ holes in the calculations.

7.1.2 Manually determine the position, *r*, of each nanoparticle relative to the center of the nanohole (*i.e.,* the displacement) where it was deposited (Figure 2b).

7.2 Determine the particle count versus displacement histograms using a standard spreadsheet program.

7.3 Calculation of the particle density: ρ = *N* (Number of Particles)/Unit Area (μm^2):

7.3.1 First, determine the annular area of a ring with a fixed width *(≈R/10,* where *R* is the radius of the hole) and bounded by two radii (r_1, r_2) at a displacement of *r* (=(r_1+r_2)/2); $A = \pi(r_2^2 - r_1^2)$.

7.3.2 Sum the number of particles, *N*, in the area from the histogram constructed in step 7.2,

above.

7.3.3 Repeat the procedure as a function of *r* to generate about 10 equal steps terminating at *r* = *R*, the hole radius.

7.4 Fit the particle density versus the displacement data to a Gaussian curve using a nonlinear least squares procedure (Figure 2a, inset)[20]. Extract the standard deviation of displacement ($\sigma_{deposition}$) for the deposition and its fitting uncertainty.

7.5 Repeat the above procedure for the SEM patterns obtained after the photoresist reflow using an SEM image shown in Figure 2c.
NOTE: After the reflow holes disappear, draw best-fit horizontal and vertical lines on GNP positions to determine the best-fit values for the hole centers. Calculate the particle displacements as in step 7.1 and extract the combined σ_{Total} following the protocol delineated in steps 7.2-7.4.
NOTE: Here, combined or total refers to the overall displacement of GNP due to the deposition and reflow steps.

7.6 Determine the fill fraction by estimating the ratio of the number of filled holes to the total number of holes, Figure 2b.

REPRESENTATIVE RESULTS:
Figure 2 (Insert Figure 2 here) shows an SEM image of 20-nm GNPs deposited in 80-nm diameter holes patterned in a 60-100 nm-thick PMMA film driven by electrostatic funneling. As observed by others[22], the process resulted in about one particle per hole. The distribution of particles around the center of the holes was Gaussian (top right inset). Most holes (93%) contained one GNP, and 95% of these particles occurred within 20 nm of the center. Further optimization, discussed elsewhere, is needed to improve the fill-fraction and the centering of the GNPs[20,25]. Figure 2b and c shows SEM images of the deposited GNPs from larger regions of the wafer, before and after the reflow of the photoresist. The discussion section presents further quantitative analysis.

The evaporative deposition could reduce the 24-48 h required for deposition[25]. When dispersions of nanoparticles were allowed to evaporate on the patterned surface, GNPs deposited on the PMMA film, as well as in holes. Mild ultrasonication in a buffered solution removed weakly bound GNPs on the PMMA, leaving only the strongly bound particles in the holes. Figure 3 illustrates how multiple particles could be forced into holes using this method because of the reduced inter-particle repulsion in the progressively concentrated ionic dispersion. Such ionic screening effects should be avoided, since they allowed multiparticle occupancy and lowered efficiency of the electrostatic funneling that directs the particle to the center of the hole. Lowering the concentration of GNPs in the depositing dispersion, along with ultrasonication, would potentially allow for the deposition of one particle per hole more rapidly than the bulk solution-phase deposition (Insert Figure 3 here). In this work, we did not optimize the necessary conditions.

The cross-sectional SEM profile displayed the hole sidewalls tilted towards their centers. The angle of the sidewall was less than the optimal 90°, creating an increasing cross-sectional area in the well upon approaching the photoresist-wafer interface. This configuration explains the observed packing pattern (left) of particles, indicating their displacement away from the center of the hole. Better focussing of the E-beam, below the interface between air and the photoresist film, would eliminate such an artifact.

Thin, solid films of PMMA photoresist[28-31] liquify and flow near the glass transition, T_g, of 110 ^{o}C. A temperature 10° below the T_g of the photoresist polymer, PMMA, initiated a slow reflow of the photoresist. In the softened, liquid-like, glassy state, the surface tension of the photoresist film reduced the edge curvature and roughness, resulting in a suppression of LER effects. The advancing liquid photoresist front completely engulfed nanoholes, along with the deposited GNPs, as illustrated in Figure 4, where the number of GNPs per hole was high (Insert Figure 4 here). Note how the photoresist reflow from the hole borders erased the pattern of nanoholes in the film. Nonetheless, strongly bound GNPs locked into the positional registry of the pattern. Remarkably, these photoresist-reflow studies revealed strong electrostatic binding of the citrate-capped GNPs to amine-terminated silanes. The similarity of the deposition pattern of GNPs before and after reflow supported this conclusion; see Figure 4c (*vide infra*).

The overall sequence of steps and the changes occurring in the corresponding SEM images are shown in Figure 5. (Insert Figure 5 here). In Figure 5b, the holes in the film shrank during photoresist reflow, while the engulfing process was completed in less than 3 min (Figure 5c). Oxygen plasma etched the thicker film of photoresist that overlaid on top of GNPs, exposing them to air. Once exposed, these GNPs were wet-etched using gold etching solution based on KI/I_2 (Figure 5d). The coefficient of variation for the diameters was 9% for the hole formed by the GNP-assisted process. Note that in these studies, the starting diameter of the holes shrank from 80 to 20 nm, which illustrates the strength of the approach. The primary limitation of the method is the introduction of uncertainty in the position of a recreated hole center due to a combination of uncertainties introduced during the GNP deposition and the resist reflow. Current ongoing work attempts to address these effects. Besides gold, other nanoparticles of different materials, such as silica (etchable in dilute HF), can be used to reduce materials and processing costs. The primary requirement is that the nanoparticle/nanostructure must be selectively etchable without affecting the resist material.

FIGURE LEGENDS:

Figure 1. Schematic representation of the strategy to remove the effects of shot-noise and line-edge roughness for the patterning of contact holes using NPs of precise size. Here, the critical dimension (CD) is the desired diameter of the holes. The approach (step 1) begins with depositing a self-assembled monolayer (SAM) of silane molecule bearing positively charged amine groups on the oxide surface of a silicon wafer. Next, E-beam lithography is used to pattern the holes (steps 2and 3) in PMMA photoresist film, the blue layer, which generates shot-noise, as illustrated in the inset SEM image. Lithography exposes amine groups at the bottom of the holes. Step 4 entails the aqueous phase deposition of controlled-size, citrate-

capped (negatively charged) gold nanoparticles (GNPs) in lithographically patterned holes using electrostatic funneling (EF). In step 5, heating the wafer to 100 °C, below the glass transition temperature of the PMMA, 110 °C, causes the reflow of the photoresist around pre-deposited nanoparticles. Etching overlaid PMMA with oxygen plasma (step 6) exposes the GNPs, and subsequent wet-etching (iodine) of the exposed particles (step 7) creates holes corresponding to the size of the GNPs. When coupled with reactive-ion/wet-etching, it is possible to transfer the hole pattern in the photoresist to SiO_2 (step 8)[32]. Reprinted with permission from Reference 20.

Figure 2. a) 20-nm diameter GNPs deposited in 80-nm diameter holes separated by a pitch, *P,* of 200 nm (top left inset). 93% of the holes contain one nanoparticle, and 95% of the nanoparticles are within 18 nm from the center (blue circle). The top right inset shows a Gaussian distribution of the particle displacement from the center, with σ = 9.0 ± 0.1 nm[33]. b) SEM image of a large area after deposition, σ = 9 ± 1 nm. c) Same as b) after the reflow of the photoresist, σ = 11 ± 2 nm. Modified with permission from Reference 20.

Figure 3. Deposition of GNPs during an evaporation lasting more than 20 min. The bottom SEM micrographs show top-down and cross-sectional views of holes patterned by E-beam. Modified with permission from Reference 25.

Figure 4. The positions of the deposited GNPs are relatively insensitive to the reflow of the photoresist (see the text). Patterns of the deposited 60-nm GNPs in 250-nm holes: a) before reflow, b) after partial reflow, and c) after complete reflow.

Figure 5. SEM. Images collected during the steps employed to minimize the variation of hole sizes. a) Deposition (24 h). b and c) Reflow of the photoresist (20 s, 3 min). d) Etching PMMA (O_2 plasma: 55 s) and GNP (wet-etch with I_2/KI solution: 10 min).

DISCUSSION:

Shot-noise (SN) in lithography is a simple consequence of statistical fluctuations in the number of photons or particles (N) arriving in a given nano-region; it is inversely proportional to the square root of a number of photons/particles:

$$SN \propto 1/\sqrt{N} \propto 1/\sqrt{A} \propto 1/r$$

where *A* and *r* are the area and the size of the exposed region, respectively. For example, when using an ArF 193-nm (6.4-eV) excimer laser to pattern 50-nm holes, the number of photons received is approximately 1×10^6 at the exposure dose of 52 mJ/cm^2. For a 50-keV E-beam source, the number of electrons delivering 50 mJ/cm^2 would be about 128, implying that the effect of SN would be 100 times greater for E-beam lithography. Furthermore, the number of photons/electrons arriving in a given region decreases directly with the area of the pattern. Consequently, a large fluctuation in the size of holes that received "identical" exposure results occurs as the dimension of the hole to be crafted decreases. For the 35-nm holes shown in

Figure 1 with the 30-keV E-beam, about 1,440 electrons deliver the requisite dose of 24 μc/cm^2. To pattern 20-nm holes under identical conditions, one would need about 400 electrons, which is close to the theoretical SN limit (200 electrons) given by Moreau[34]. Currently, the only way to suppress the effect of SN is through the use of a low-sensitivity photoresist that needs a higher electron/photon dose. It comes at the cost of lower throughput and higher costs for nano-patterning. Our method reduces the effect of size fluctuations by using monodisperse nanostructures to redefine the size of the lithographically patterned holes while maintaining the original positional registry. The registry is fixed by the strong electrostatic binding of nanostructures to the surface, guided by electrostatic funneling.

The success of the patterning in this method depends on two effects. The first is the variation in the sizes of the holes, and the second is the centering of the nanoparticles within the holes that affect the positional registry. The coefficient of variation for the diameter of holes patterned through this approach (9%, or 19 ± 2 nm) is comparable to the coefficient of the size (8%) of the GNPs[20]. On the other hand, as revealed in Figure 1, the E-beam-patterned 35-nm (35 ± 9) holes, made without using this approach, had a CV of 35%. The corresponding CV of E-beam-alone patterning would become even worse when fabricating 20-nm holes. The SN can be set to be proportional to the CV, with rough estimates of CVs for 20-nm and 80-nm holes at 61% and 15%, respectively. The method presented here provides at least a six-fold (~61%/9%) improvement in CV over E-beam-alone patterning of 20-nm holes. Even starting with 80-nm holes, almost 60% improvement in CV results (~15%/9%) occurs after this approach.

The second effect concerns particle deposition away from the geometric center of the holes (registry). Two contributing factors to this effect were extracted from SEM data collected after the deposition of GNPs in holes (Figure 2b) and after photoresist-reflow (Figure 2c). The statistical analysis of the displacement of GNPs from the center of the nanoholes in which they resided (Figure 2a) revealed that during the solution-phase deposition, the distribution of GNPs about the center of the hole was Gaussian, with a standard deviation ($\sigma_{Deposition}$) of 9 nm, or roughly half the diameter of GNPs. The analysis procedure was equivalent to assuming that the particles, on average, remain at the center of holes, although individually they may be displaced randomly due to diffusion during deposition.

The second factor affecting displacement is due to the motion of GNPs during the photoresist reflow. Results, presented in Figure 4, indicate that the positively charged AATMS SAM binds so strongly to GNPs that they do not move duringthe reflow of the photoresist. A similar analysis of SEM images (*vide supra*) collected after the photoresist reflow (Figure 2c) step provided the overall standard deviation (σ_{Total}) in the particle positioning (*i.e.,* registry) after the deposition and reflow. To extract the contribution of resist reflow, we assumed that the processes of deposition and photoresist-reflow produce independent effects in displacing particles from the center of holes, such that:

$$\sigma_{Total}^2 = \sigma_{Deposition}^2 + \sigma_{\mathrm{Re}sist-reflow}^2$$

Using the fitted values of $\sigma_{Deposition}$ (9 ± 1 nm) and σ_{Total} (11 ± 2 nm), the extracted value of $\sigma_{Resist\text{-}reflow}$ was estimated to be 6 nm, which is comparable to three times the standard deviation in the 20-nm GNPs. Such a low standard deviation implies a very negligible effect on the displacement of bound particles during the photoresist reflow process. Nevertheless, the $\sigma_{Deposition}$ appears to vary directly with the size of the GNP; thus, it needs significant improvements. A model presented elsewhere[20] suggests the optimization of the charge-density of the photoresist film and SAM to improve the positional registry. Several methods, including the use of electrostatic bias and charge on GNPs, are currently being explored. Note, as discussed above, that an SEM image analysis provides a straightforward method for the above process of optimization.

The commercial availability of almost monodisperse GNP particles dictated the choice of gold nanoparticles. In principle, other inexpensive nanomaterials, such as silica nanoparticles derivatized with appropriately charged chelant, are also suitable candidates. The primary criterion for the selection of nanoparticles is their monodispersity and their susceptibility to etching. For electrostatic funneling, appropriate complementary charges on the SAM and NP must be present. The charge on NPs depends on its zeta potential, whose sign and magnitude can be tuned either through the pH of the solution or the charge on chelants. Similarly, selecting cationic or anionic terminal end groups allows for the modification of surface charge on the SAM. If perfected, the method readily extends to pattern trench lines with nanowires[35-37]. The overall success of the method will depend on optimizing the placement and filling nanostructures on pre-patterned photoresist films, exploiting electrostatic, magnetic, or ligand-ligation interactions

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DISCLOSURES:
The authors have nothing to disclose.

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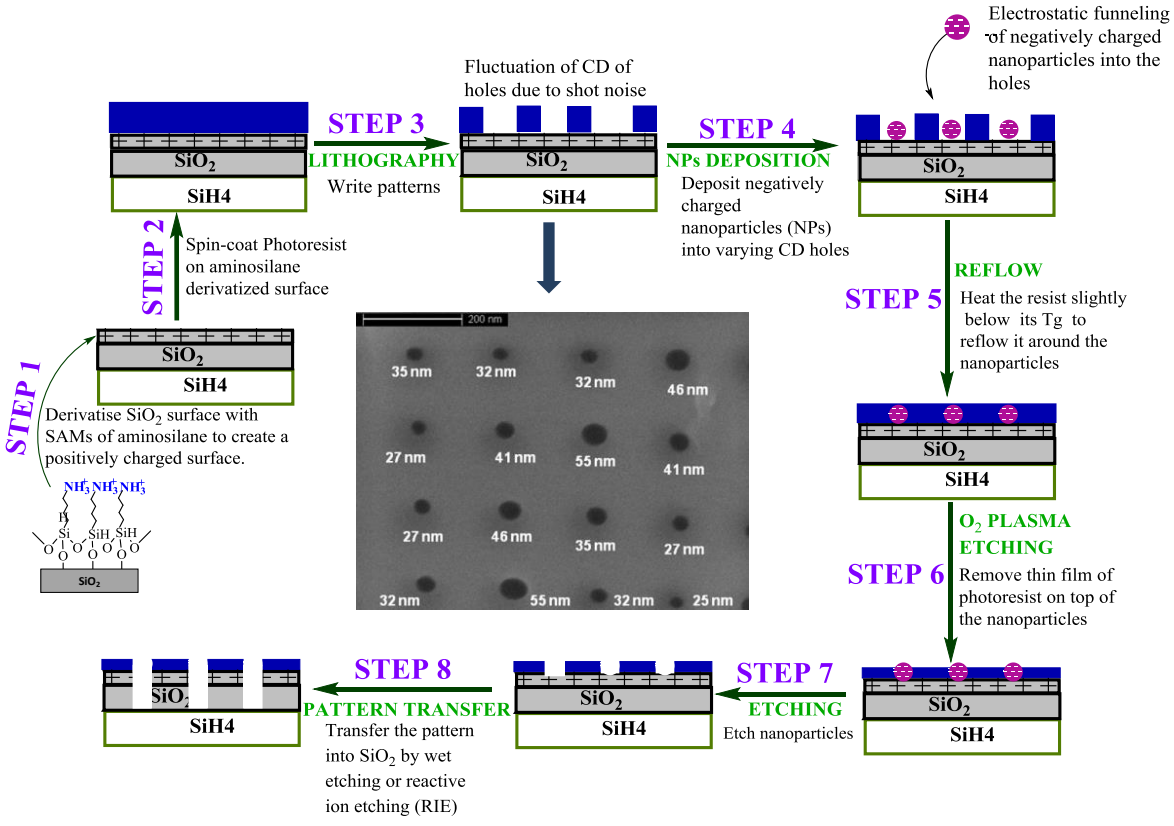

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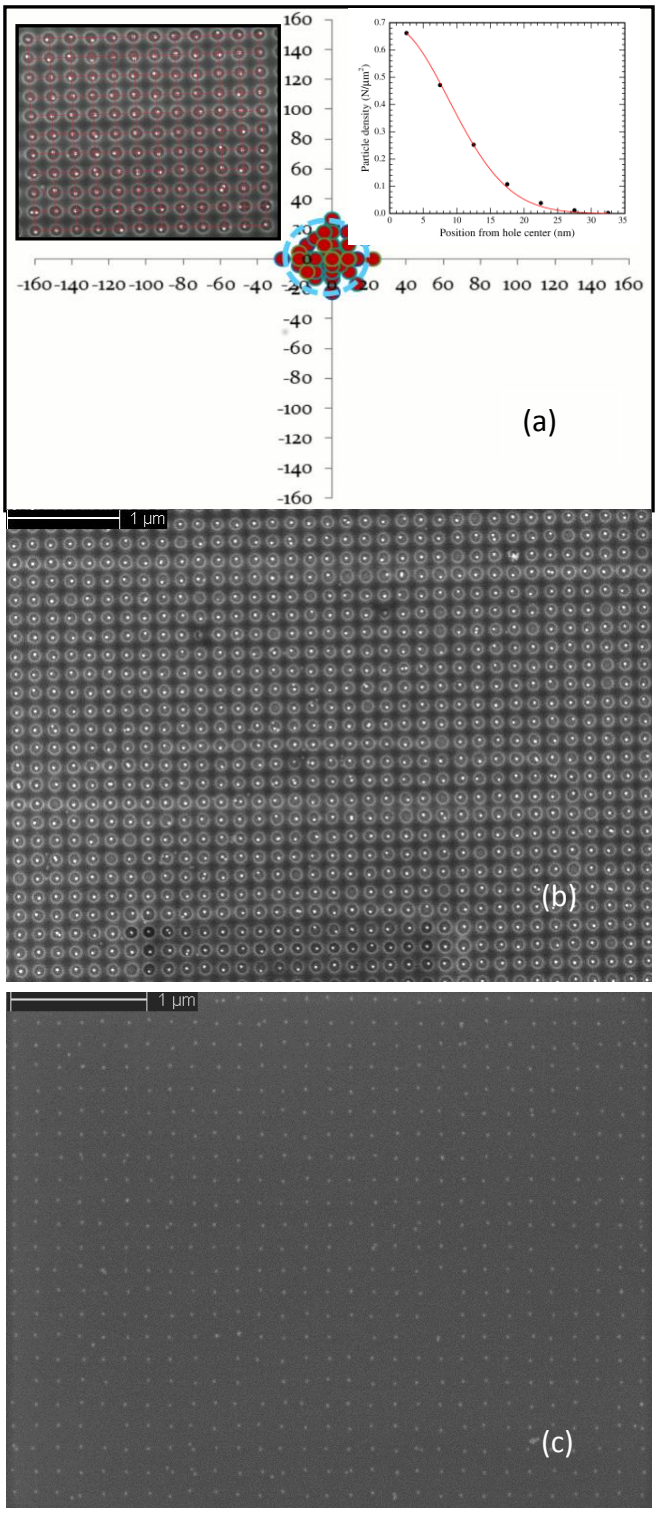

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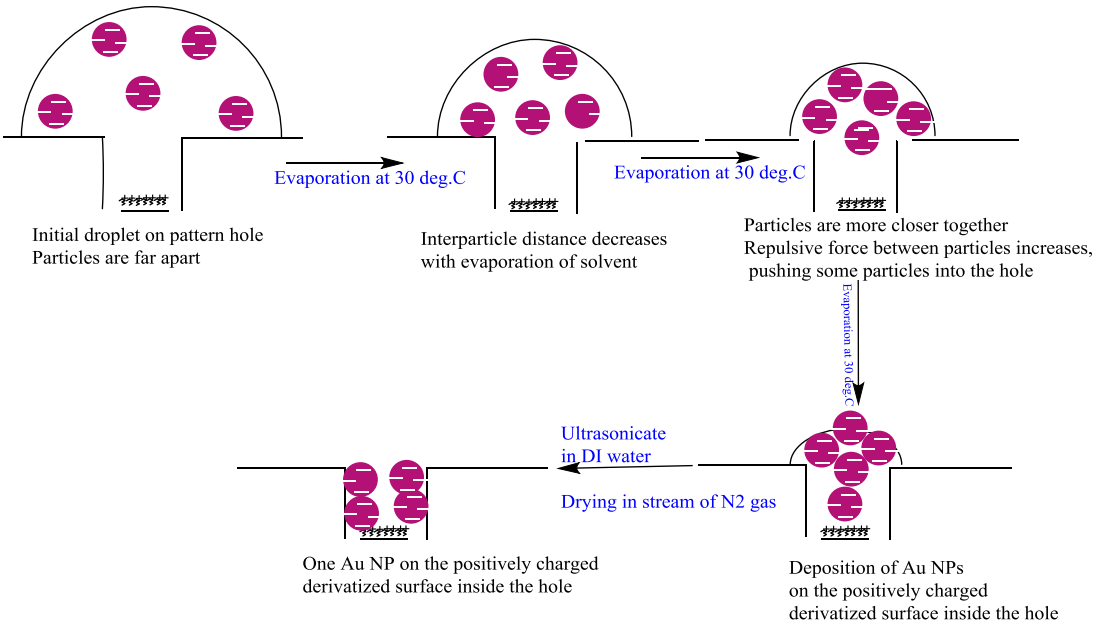

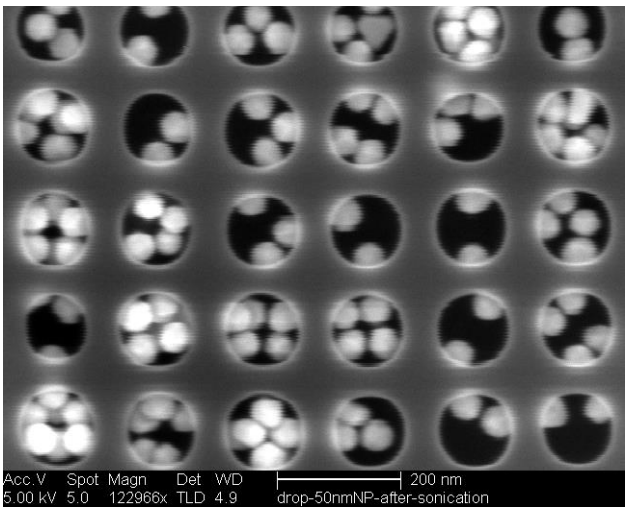

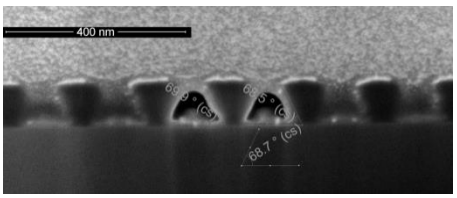

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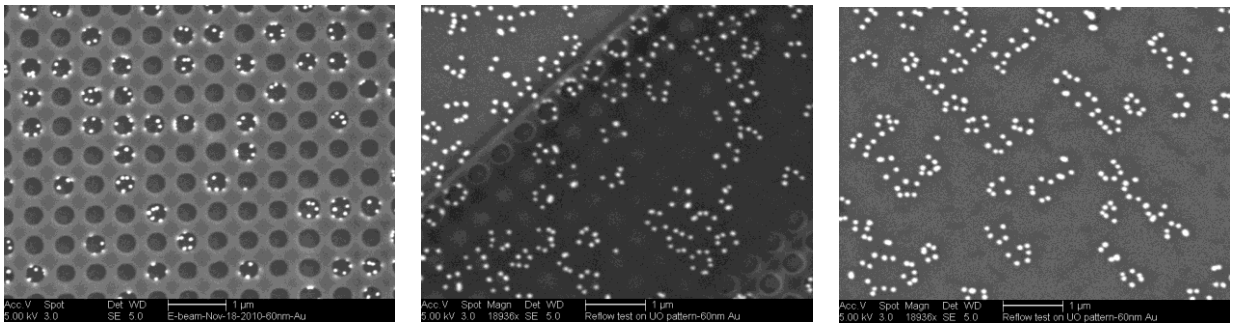
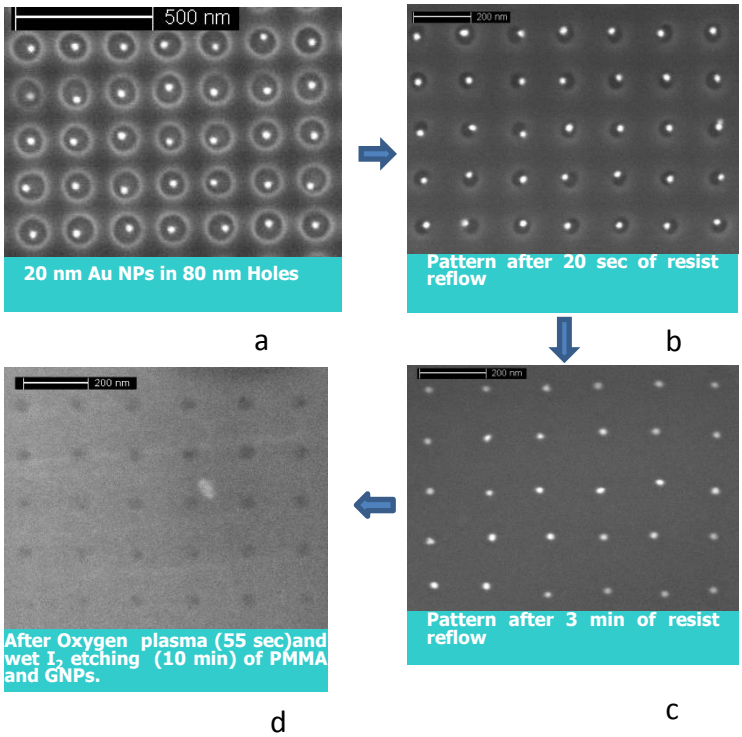


a **b** **c**

Figure 5



Excel Spreadsheet- Table of Materials/Equipment

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Name of Reagent/ Equipment	Company	Catalog Number	Comments/Description
AATMS (95%)	Gelest Inc.	SIA0595.0	N-(2-aminoethyl)-11-aminoundecyltrimethoxysil
Gold colloids (Ted Pella Inc.)	Ted Pella	15705-20	Gold Naoparticles
hydrogen peroxide	Fisher Scientific	H325-100	Analytical grade (Used to clean wafer)
hydrochloric acid	Fisher Scientific	S25358	Analytical grade
Ammonium hydroxide	Fisher Scientific	A669S-500SDS	Analytical grade (Used to clean wafer)
hydrogen fluoride	Sigma	AC27725025 0	Analytical grade(used to etch SiO2)
Toluene (anhydrous, 99.8 %)	Aldrich Sigma	244511	Analytical grade (solvent used in Self Assembly o
Isopropyl alcohol (IPA)	Aldrich Sigma	W292907	Analytical grade (Used to make developer)
Methyl butyl ketone (MIBK)	Aldrich Sigma	29261	Analytical grade(used to make developer)
1:3 MIBK:IPA developer	Aldrich Sigma		Analytical grade (Developer)
950 k poly(methyl methacylate (PMMA, 4 % in Anisole)	Aldrich	182265	Photoresist for E-beam lithography
Purified Water : Barnstead Sybron Corporation water purification Unit, resistivity of 19.0 MΩcm			Water for substrate cleaning
Gaertner ellipsometer	Gaertner		Resist and SAM thickness measurements
XPS, ThermoScientifc ESCALAB 250 instrument	Thermo-Scientific		Surface composition
An FEI Siron XL30	Fei Corporation		Characterize nanopatterns
Zeiss sigma VP FEG SEM	Zeiss Corporation		E-beam exposure and patterning

MDS 100 CCD camera	Kodak		Imaging drop shapes for contact angle measurer
Tegal Plasmod	Tegal		Oxygen plasma to etch photoresist
I2	Sigma Aldrich	451045	Components for gold etch solution
KI	Sigma Aldrich	746428	Components for gold etch solution
Ellipsometer (LSE Stokes model L116A);	Gaertner	L116A	AATMS self assembled monolayer film thickness

ane

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Article Title: Sacrificial Nanoparticles to Remove Effects of Shot Noise

Signature: S. B. Ra

Date: 1/31/2016

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Point by Point Response to the editor requested changes:

The manuscript has been extensively edited, and several sections are rewritten in response to the request by the editor.

1. Please adjust the numbering of your protocol section to follow JoVE instructions for authors, 1. should be followed by 1.1) and then 1.1.1) if necessary and all steps should be lined up at the left margin with no indentations. For instance, sections 2,3,4,5 are not written in step-wise manner.

Done.

2. Please re-write steps of your protocol section in imperative tense, as if you are telling someone how to do the technique (i.e. "Do this", "Measure that" etc.). Please try to avoid usage of phrases such as “should be”, “could be”, “would be” and write in the active/imperative style. For instance, “Clean the surface of silicon wafers…”, etc. Please ensure that all the steps are written in imperative tense.

Done.

3. JoVE is unable to publish manuscripts containing commercial sounding language, including trademark or registered trademark symbols (TM/R) and the mention of company brand names before an instrument or reagent. Please remove all commercial sounding language from your manuscript and replace it with a more generic term as much as possible throughout the entire manuscript. All commercial products should be sufficiently referenced in the table of materials/reagents. Examples of commercial sounding language in your manuscript are Zeiss sigma VP FEG SEM, Siron XL30, Tegal Corporation, etc.

Done. Vendor names now appear in the Excel file containing materials and equipment.

4. What are the action items in section 2, please discuss the details of the protocol in step-wise manner. Additionally, please see section 3, 4, 5, step 7.1 and 6.2.

Done.

5. Please provide all the details and please ask yourself the how question in order to provide more details.

Done.

6. Please include spaces between all numbers and units.

Done

7. Please use “sec” as the abbreviation for second(s), “min” for minute(s) and hr for hrs or hour(s) when it is next to a number.

Done.

8. After you have made all of the recommended changes to your protocol (listed above), please re-evaluate the length of your protocol section. There is a 10 page limit for the protocol text, but there is a 3 pages limit for filmable content. If your protocol is longer than 3 pages, please highlight (in yellow) 2.75 pages (or less) of text to identify which portions of the protocol are most important to include in the video; i.e. which steps should be visualized to tell the most cohesive story of your protocol steps. Please see JoVEs instructions for authors for more clarification. Remember that the non-highlighted protocol steps will remain in the manuscript and therefore will still be available to the reader.

Done.

9. Please remove the embedded figures from the manuscript. Figure legends, however, should remain within the manuscript text, directly below the Representative Results text.

Done.

10. Each figure or data table must have an accompanying legend including a short title, followed by a short description of each panel and/or a general description. All figures showing data must include measurement definitions and error bars (if applicable). Please include the figure legends as part of the manuscript text (not part of the figure file) directly below the representative results text.

Done

11. If your figures and tables are original and not published previously, please ignore this comment. For figures and tables that have been published before, please include phrases such as “Re-print with permission from (reference#)” or “Modified from..” etc. And please send a copy of the re-print permission for JoVE’s record keeping purposes.

Figures 1 and 2 have appeared elsewhere. I have initated a process of getting the permission to use these figures from the RSC.

12. Please make sure that the “Discussion” is written under the following sections.
a. Critical steps within the protocol.
b. Modifications and troubleshooting.
c. Limitations of the technique.
d. Significance of the technique with respect to existing/alternative methods.
e. Future applications or directions after mastering this technique.

Done.

13. Please copyedit the entire manuscript for any grammatical errors you may find. The text should be in American-English only. This editing should be performed by a native English speaker (or professional copyediting services) and is essential for clarity of the protocol and the

manuscript. Please thoroughly review the language and grammar prior to resubmission. Your JoVE editor will not copy-edit your manuscript and any errors in your submitted revision may be present in the published version.

Done.

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Endnote software package with the JoVE style file was used to format references.

15. References – Please abbreviate all journal titles.

Unfortunately, JoVE style file did not automatically abbreviate the journal titles. Therefore, I have manually abbreviated the titles.

16. NOTE: Please include a line-by-line response letter to the editorial and reviewer comments along with the resubmission.

•NOTE: Please download this version of the Microsoft word document (File name: 54551_R1_070516) for any subsequent changes.

•Many steps require additional detail:

-1.2.1 – What do xx and yy stand for? What values should be used? (**Corrected/Text added**)

-1.3.1, 3.5 – What sonication settings were used?(**Corrected**)

-Section 1.4 – Please provide citations for each method mentioned in 1.4.1, 1.4.2, and 1.4.3. (**Citation added**)

-2.1 – How long is spinning performed? (**Text corrected**)

-2.3 – How is film thickness measured? (**Text corrected)**

-2.4 – What pattern is used here? (**Poker dot**)

-3.1, 3.3 – Please describe the GNP solutions. How many? What concentration and components? What size of GNP can be used? (**Corrected**)

-3.2 – In what way does size influence length of incubation? Does smaller size mean longer incubation? (**Text modified**)

-3.3 – How are GNPs sprayed? (Nozzle size, orientation of spray, quantity sprayed, etc.).(**Corrected**)

-3.4 – What is used for incubation? A hot plate? An incubator? (**On a hot plate; text modified**)

-4.3 – Please describe how this is performed. How are the holes identified? How are the cross-section images obtained? (**Corrected and clarified**)

-Section 7 – Are images acquired of the etched film from Section 6 prior to these calculations? If so, please describe how these images are acquired.(**corrected**)

-7.1.1 – Is this performed in software or by hand? (**By hand**)

-7.2, 7.3, 7.4, 7.6 – How is this performed? How is the number of holes obtained? Before or after etching? (**Section modified to clarify the analysis procedure**)

•Formatting:

-Please re-write the title to reflect the procedure. We suggest “Use of nanoparticles….” (**Corrected**)

-Please include a space between 1.4 and 1.4.1, 7.1 and 7.1.1, etc.(**corrected**)

-2.2 – Please correct the font.(**Corrected**)

-4.2 – Should sputter-coating be performed before SEM (4.1)? **(Sub-section modified to clarify strandard top-down and cross-sectional imaging**)

-References – Please abbreviate journal titles. (*Done; But please verify if I missed any abbreviations)*)

•*Length of highlighted material is below the 1 pg minimum* limit for filming. Please highlight additional material to be filmed for the video. We suggest highlighting sections 1, 2, & 4. (Corrected; except for section 2, as this would require travel to Eugene, OR)

•Grammar:

-Line 38 – "the effects shot noise" **(Text corrected)**

-3.1, 3.3, 7.4 – Please use a complete sentence in the imperative tense. **(Text corrected)**

-7.3.1 – Please use imperative tense. **Text corrected**

-6.1 – "GNPS" **(Text corrected)**

-2.4.1 – "distribution of particle" **(Text corrected)**

-Line 341 – Should be "conditions, one would need" **(Text corrected)**

-Line 354 – "Figures 1" **(Text corrected)**

-396 – "for selection nanoparticles" **(Text corrected)**

•Discussion: Please discuss the limitations of the protocol. (Added)

Response to Editorial comments:

•NOTE: Please download this version of the Microsoft word document (File name: 54551_R2_071316) for any subsequent changes. Please keep in mind that some editorial changes have been made prior to peer review.

•Please keep the editorial comments from your previous revisions in mind as you revise your manuscript to address peer review comments. For instance, if formatting or other changes were made, commercial language was removed, etc., please maintain these overall manuscript changes.

•One step requires additional detail: 2.3 – Please provide a citation or cite manufacturer's instructions. (Done)

More instrumental details have been added to the materials template excel spreadsheet.

•Formatting:
-Please include a space between 1.4 and 1.4.1, 7.1 and 7.1.1, etc.

Done.
-Please number steps sequentially. For example, step 3.1 is followed by 3.3, 7.3.4 follows 7.3.2, etc.

(Done)

•Grammar:
-Please correct the capitalization in the title.

Done.
-3.3.1 – "To deposit of GNPs by evaporation"

Done
-"a SEM" should be "an SEM" ????

•Branding: 2.3 - Gaertner
Done.
•Discussion: Please discuss the limitations of the protocol.

Lines 399-441 present discussion of advantages and limitations of the protocol along with the factors affecting it.

•If your figures and tables are original and not published previously, please ignore this comment. For figures and tables that have been published before, please include phrases such as "Re-print with permission from (reference#)" or "Modified from.." etc.

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Done.

•IMPORTANT: Please copy-edit the entire manuscript for any grammatical errors you may find. The text should be in American-English only. This editing should be performed by a native English speaker (or professional copyediting services) and is essential for clarity of the protocol and the manuscript. Please thoroughly review the language and grammar prior to resubmission. Your JoVE editor will not copy-edit your manuscript and any errors in your submitted revision may be present in the published version.

Done.

•NOTE: Please include a line-by-line response letter to the editorial and reviewer comments along with the resubmission.

Done.

Reviewer #1:

Manuscript Summary:

N/A

Major Concerns:

N/A

Minor Concerns:

N/A

Additional Comments to Authors:

The article is interesting and deserves publication. Though, there are recommendations of minor improvements: 1) Whereas is Figure 1 a detailed measurement of hole sizes is presented this is not done for the result obtained in Figure 5. The quality of the SEM photo in Fig. 5d after Oxygen plasma and wet I2 etching is not allowing a meaningful comparison.

Since the GNP size is 20 nm, the thickness of the photoresist film after the O_2 plasma etching is less than 20 nm. Thus, removal of 80 nm thick portion of the resist film (out of initial 100 nm thick film) is necessary so that GNPs are exposed to the I_2 etch solution. Such a thinned PMMA resist film (Figure 5c and 5d) is a very delicate and is affected by the process of SEM imaging itself, reducing the contrast and the edge definition. This would not be the case for other chemically amplified resist showing higher etch resistance than PMMA.

Further, as obvious from Figure 5c there are large deviations of the gold particle positions from the desired position. This probably is due to the fact that 20nm diameter gold particles were used for 80nm diameter pattern holes. This leads as shown in Figure 3 to multiple gold particles within the 80nm diameter pattern holes.

We agree.

Therefore the wording "One Au NP on the positive charged derivative surface inside the hole" is desirable but not shown in the drawing and also not in the SEM images.

The proposed innovation might work if the size of the gold particle is such that indeed only a single gold particle is fitting inside the pattern hole, e.g. for 80nm diameter pattern holes the diameter of the gold particle should be more than 40nm.

We agree that this would be desirable. Our objective here was to show that even 4X nanoparticle diameter contact holes could be repaired. The method would be expected to work even better when the hole size is closer to the particle size.

Further, the method is shown with PMMA resist for which a very high exposure dose is needed. A EUV or e-beam industrial application would work with a resist (e.g. pCAR) having much lower dose and thus exhibiting much more prominent shot noise

influendes. With this, the benefit of the innovation could be presented more clearly. Though, as this would mean more major work probably not possibile within the present funded project, such recommendations might be mentioned in the minor revision of the article.

We agree with this excellent suggestion. This would be a subject of our future studies.

Reviewer #2:

Manuscript Summary:

Overall, the authors provided a detailed procedure, steps need special attention, and results analysis of this technique using sacrificial nanoparticles to remove effect of shot-noise in contact holes. Clear background and rationale are also provided. Therefore, publication is recommended. In addition, the authors may want to consider the following minor suggestions.

Major Concerns:

N/A

Minor Concerns:

1) The authors may want to provide details of Fig 4, like dimensions of GNPs and holes. Moreover, it's not very clear from Fig 4a~c that GNPs didn't move
after photoresist film reflow. The authors may want to provide more analysis results to support this conclusion.

We agree. The gold NP and hole sizes are 60 nm and 250 nm, respectively. The gold particles do move, about 6 nm during resist reflow based on our analysis of 20 nm particles deposited in 80 nm holes (lines 421-445). We suspect that the RMS displacement of larger particles such as those shown in figure 4 would be smaller due to their stronger binding that should scale as their contact area on the underlying substrate.

2) Line 319 "4c" and line 321 "4d" should be "5c", "5d".

Corrected.

Additional Comments to Authors:

N/A

Reviewer #3:

Manuscript Summary:

This manuscript presented a promising approach to reduce the SN effects in next-generation litho. The experimental data and discussion are solid and well organized. I would like to recommend this manuscript for publication.

Major Concerns:

N/A

Minor Concerns:

For the cost reduction in industry, is it possible to use other NPs of cheaper metals instead of gold? Could you briefly summarize possible candidates and the technical problems (stability, charge etc.) with them?

The requested information now appears near the end of the manuscript.

Additional Comments to Authors:

N/A