

Fabrication of Gold Nanoparticles Using E-beam Lithography: Effect of Development Conditions on Shape and Resolution

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Abstract and Introduction:

Due to the short wavelengths of electrons relative to those of the light photons used in optical lithography, electron beam lithography (EBL) is an extremely high-resolution lithographic process. Importantly, however, the overall resolution achieved is greatly affected by the development conditions used.

The purpose of the work described in this paper was to determine the optimal development conditions for the fabrication of rectangular gold (Au) nanoparticles via EBL.

Silicon (Si) wafer substrates were coated with a polymer resist (PMMA) prior to exposure to the electron beam used to write the desired pattern via EBL. Following exposure, the substrates were developed. The developers tested were solutions comprised of different mixtures of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA), ranging from a MIBK:IPA ratio of 1:3 (v/v) to pure IPA. The 1:3 MIBK:IPA is a common developer that produces high-resolution samples with small feature sizes.

Pure IPA was chosen as a developer based on the results of Yasin [1], which yielded higher-resolution samples than those developed using 1:3 MIBK:IPA.

Experimental Procedure:

Hollow, rectangular, Au nanoparticle arrays were fabricated using a JEOL JBX-9300FS 100kV electron beam lithography (EBL) system. The substrates were pieces of Si wafers approximately $3 \times 3 \text{ cm}^2$. The array consisted of 42 windows, each measuring $300 \times 300 \mu\text{m}^2$. Each window contained an array of thousands of particle pairs with varying interparticle separations. The desired outcome was the production of homogeneous particles that measured $180 \times 240 \text{ nm}$ and contained hollow centers $60 \times 120 \text{ nm}$ in area. To prevent unwanted interactions between particle pairs, every particle pair was spaced $1 \mu\text{m}$ from the next. All particle and pattern parameters were specified while writing the files for the EBL system.

To prepare the Si substrates for exposure, they were rinsed with acetone, dried with N_2 , spin-coated with 80 nm

of poly(methyl methacrylate) (PMMA), and baked for two minutes at 180°F . The substrates were patterned using electron beam doses of $500\text{-}3500 \mu\text{C}/\text{cm}^2$ at 2 nA.

Following exposure, the samples were developed to remove the exposed patterns. During the development process, the following ratios of solutions containing MIBK (methyl isobutyl ketone) and IPA (isopropyl alcohol) were tested to optimize resolution: 1:3 MIBK:IPA, 1:5 MIBK:IPA, 1:7 MIBK:IPA, and pure IPA.

All the samples, except for the pure IPA sample, were developed for 10 seconds in the above solutions followed by a rinse in IPA for 30 seconds. The pure IPA sample was developed for 40 seconds. A CVC electron beam evaporator was then used to deposit a 0.5 nm chromium (Cr) adhesion layer ($0.1 \text{ \AA}/\text{s}$) followed by a 22 nm layer of Au ($0.5 \text{ \AA}/\text{s}$). Finally, the remaining resist was removed by soaking the wafer in 1165 for approximately 4.5 hours. The samples were imaged using scanning electron microscopy (SEM).

Results and Conclusion:

The initial base dose used for fabrication was $3500 \mu\text{C}/\text{cm}^2$. It was apparent upon examination of the substrate, via SEM (LEO 11530 FE-SEM) at 8 kV accelerating voltage using a secondary detector, that the particles were overdosed causing the exposure of a wider pattern than specified. Particle dimensions became progressively more accurate as the base dose was modulated to $1000 \mu\text{C}/\text{cm}^2$ (see Figure 1).

Changes in particle resolution due to development conditions were determined using SEM images taken on the Zeiss Ultra 60 FE-SEM at 10 kV accelerating voltage using a secondary electron detector by Rachel Near (see Figure 2). Resolution was measured based on the linearity of the particles edges and the measure of perpendicularity of the vertices (corners).

The resolution trended as predicted, with the 1:3 MIBK:IPA sample having the highest resolution followed by the 1:5 MIBK:IPA sample, and the 1:7 MIBK:IPA sample producing the poorest-resolution samples.

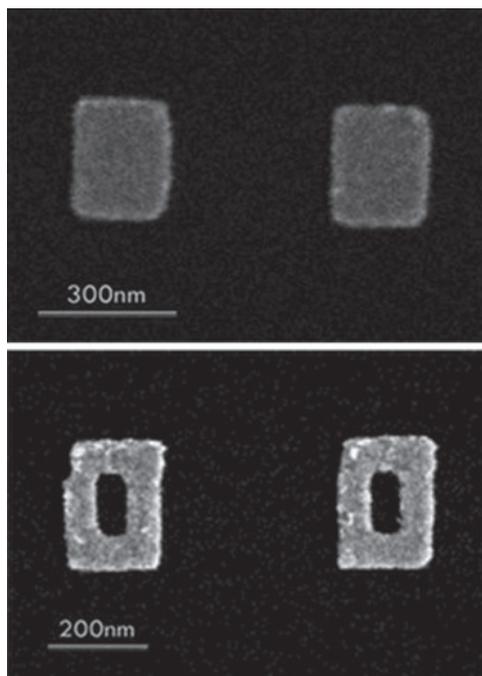


Figure 1: Comparison of overdosed particle with base dose of $3500 \mu\text{C}/\text{cm}^2$ (L) and accurately dosed particle with base dose of $1000 \mu\text{C}/\text{cm}^2$ (R).

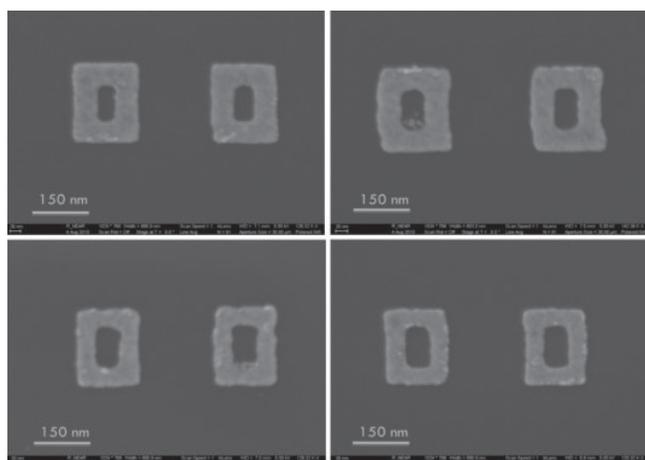


Figure 2: Results of varied developers on particle resolution. 1:3 MIBK:IPA top left, 1:5 MIBK:IPA top right, 1:7 MIBK:IPA bottom left, Pure IPA bottom right.

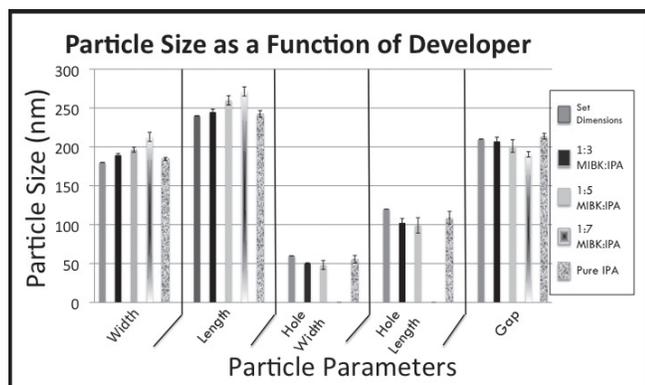


Figure 3: Graph of particle size accuracy.

Surprisingly, the pure IPA sample produced much better resolution than anticipated and actually had a resolution comparable to that obtained with the 1:3 MIBK:IPA sample.

To provide a quantitative measure of the particle size accuracy, the particle parameters were measured using images taken on the Leo SEM (see Figure 3). The pure IPA sample had measurements that were closest to the specified particle dimensions.

Based on the foregoing results, the 1:3 MIBK:IPA and pure IPA outperformed both 1:7 and 1:5 solutions of MIBK:IPA. While pure IPA produced particles with sharper edges, corners, and centers as well as more accurately sized particles, 1:3 MIBK:IPA had a higher ratio of particles that were actually hollow. IPA thus appears to be a viable option as a developer, producing very accurately sized particles of satisfactory resolution.

Future Work:

Further experimentation using IPA as a developer is necessary. Future research should also vary the development time to further optimize resolution. Nonetheless, the particle resolution is adequate for characterization of their optical properties as a function of size, shape, orientation, and interparticle spacing.

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References:

[1] Shazia Yasin, D.G. Hasko, H. Ahmed. "Comparison of MIBK/ IPA and water/IPA as PMMA developers for electron beam nanolithography," Microelectronic Engineering. Volumes 61-62, 745-753, 2002.