

Patterned Arrays of Gold Nanoframes Using High Resolution E-Beam Lithography

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Abstract

Nanostructures of various geometries offer unique optical and catalytic properties. Such structures are typically synthesized in solution, which rely on surfactants to prevent their aggregation; however, these surfactants can dampen the catalytic potential of the nanostructure. By synthesizing the nanostructures on a substrate they can be immobilized, allowing easier handling and improved catalytic ability. Using nanolithography techniques, we are attempting to pattern arrays of ultra-thin gold nanoframes. Employing the photoresist poly(methyl methacrylate), (PMMA), we can use e-beam lithography to create pedestals of PMMA protected silver with complex and unique shapes, allowing for the controlled deposition of gold. The resulting gold nano-frames can then be characterized by their optical and catalytic properties, such as the reduction of 4-nitrophenol to 4-aminophenol by borohydride.

Keywords: Nano-lithography, nanostructure, electron beam lithography, gold, nanoframe

I. Introduction

Metal nanostructures have been shown to possess unique catalytic^{2,3,23}, sensing^{4,5,6}, and plasmonic¹ properties. These abilities can be tuned by changing the size, shape, and dielectric environment¹ of the metal nanoparticles. Surfactants and ions are frequently used to control the morphology of these nanoparticles,^{7,8} and to prevent aggregation⁹; however, these surfactants can alter the properties (e.g. catalytic activity) of the nanoparticles.¹⁰

Nano-frames have been successfully synthesized in solution utilizing surfactants; however, these structures can degrade over time and lose their distinctive shapes. The synthesis of such nano-frames in solution is dependent upon the facets of the template structure that a metal favorably reduces onto, with the template being subsequently removed by chemical etching or galvanic replacement.¹²⁻¹⁶ Frames of sub-10 nm widths have been obtained from synthesis in solution and have shown remarkable optical properties as well as impressive catalytic ability.

Here, patterned arrays of Au nanostructures supported on a soda-lime glass substrate are constructed using e-beam lithography techniques. These techniques for nanostructure construction possess the advantage of (i) being immobilized on a substrate, thereby avoiding the possibility of any aggregated nanostructures, (ii) high density arrays of nanostructures with complex and unique geometries, and (iii) the implementation of PMMA as a photoresist, which is readily available compared to similar photoresists, most of which are sensitive to ambient light and require special precautions.²⁰ The assembly of the nanostructures is a six-step process of bottom-up and top-down techniques that utilize a PMMA layer to selectively etch areas of exposed Ag and controllably reduce Au on the edges of exposed silver structure. Our study focuses on creating a simple and novel process for assembling patterned arrays of ultra-thin Au nanoframe structures; furthermore, to then study their distinct optical and catalytic functionalities.

Experimental

a) Materials and reagents

Poly(methyl methacrylate) average $M_w \sim 15,000$ by GPC, toluene (anhydrous, 99.8%) and platinum(IV) chloride (96%) were purchase from Sigma-Aldrich. Isopropanol (HPLC grade, 99.9%), ammonium hydroxide (29%, certified ACS plus), hydrogen peroxide (30%, Certified ACS), and Fisherbrand™ plain glass microslides were purchase from Fisher Scientific.

The PMMA solutions used for layering were prepared by dissolving powder PMMA with toluene.

b) Sample preparation

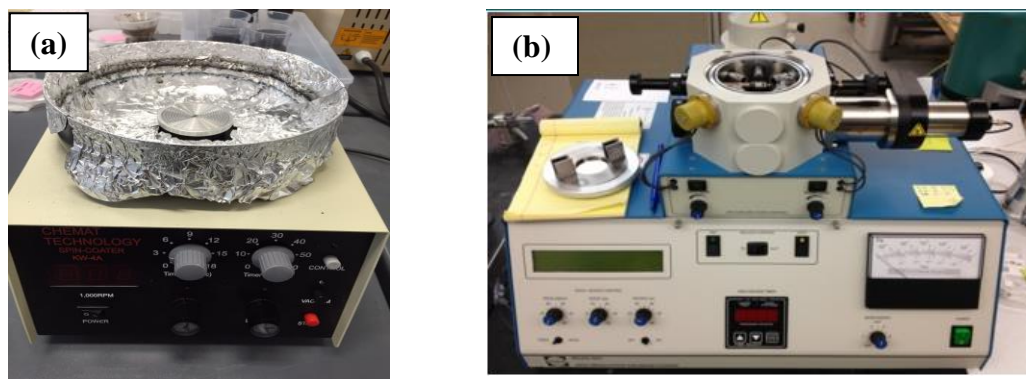


Figure 1. – (a) KW-4A Spin Coater for PMMA layer and (b) Gatan Ion Beam Coater Model 681 Sputter Coater for silver sputtering.

Ag thin films (100 nm) were sputter coated onto soda-lime glass substrates ($1 \times 1 \text{ cm}^2$) using a Model 681 Gatan Ion Beam Coater (Fig. 1b). The silver coated substrates were then immediately placed on the spin-coating stage (Fig. 1a) and held by vacuum for PMMA layering. Three drops of PMMA solution (either 2% or 10%) were placed on the sample, followed by initialization of the spin process. After spin-coating, the samples were given a post-bake treatment by heating at 165°C for 10 minutes in order to evaporate excess toluene.

c) E-beam writing and processing

Following PMMA layering, the samples were anchored onto an SEM stub using carbon tape and placed in the SEM chamber. Before writing, the e-beam was focused with ~5000x magnification at the corner of the sample to ensure high resolution when writing (ultra-high resolution can be achieved by additional steps).¹⁹ The desired patterns were then drawn using the SEM, with arrays ranging from 5x5 to 10x10 of sub-5 μm structures. The optimal exposure parameters were found to be a dwell time of 25 μs and a pitch of (30x30) nm.*

The exposed PMMA was developed in a 3:7 isopropanol:water solution (by volume) for 3-15 seconds – checking the development intermediately using an optical microscope. Once the pattern is completely visible, the exposed silver was then chemically etched using a 1:1 $\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$ solution (by volume).

Platinum was then deposited by placing the sample in a solution of 50 μM ascorbic acid and 100 μM NaOH at 90°C for 1 min, followed by the 1 mL addition of 50 μM H_2PtCl_6 solution. The sample was left in the solution for 5 min before being taken out and washed with DI water. Subsequently, the PMMA layer can be removed using acetone, and the remaining silver etched as previously described.

**The author acknowledges that the exact current of the e-beam is not stated and will be measured as soon as possible.*

II. Results and Discussion

PMMA solutions of 2% and 10% were used for e-beam lithography to determine the optimal PMMA layer thickness for high-resolution and stability during development, silver etching, and Au/Pt deposition.

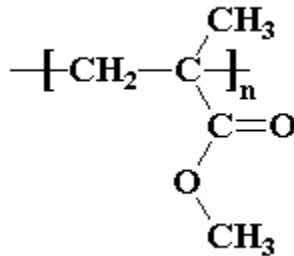


Figure 2. Chemical structure of the polymer poly(methyl methacrylate) used as a photoresist in e-beam lithography.

Spin-coating settings of 5s at 500 rpm for stage one and 50s at 3000 rpm for stage two, yielded film thicknesses of ~100 nm and ~1000 nm for 2% and 10% PMMA, respectively. The resulting layer thickness of the 2% PMMA solution was unable to maintain structural integrity through all of the chemical processing steps.

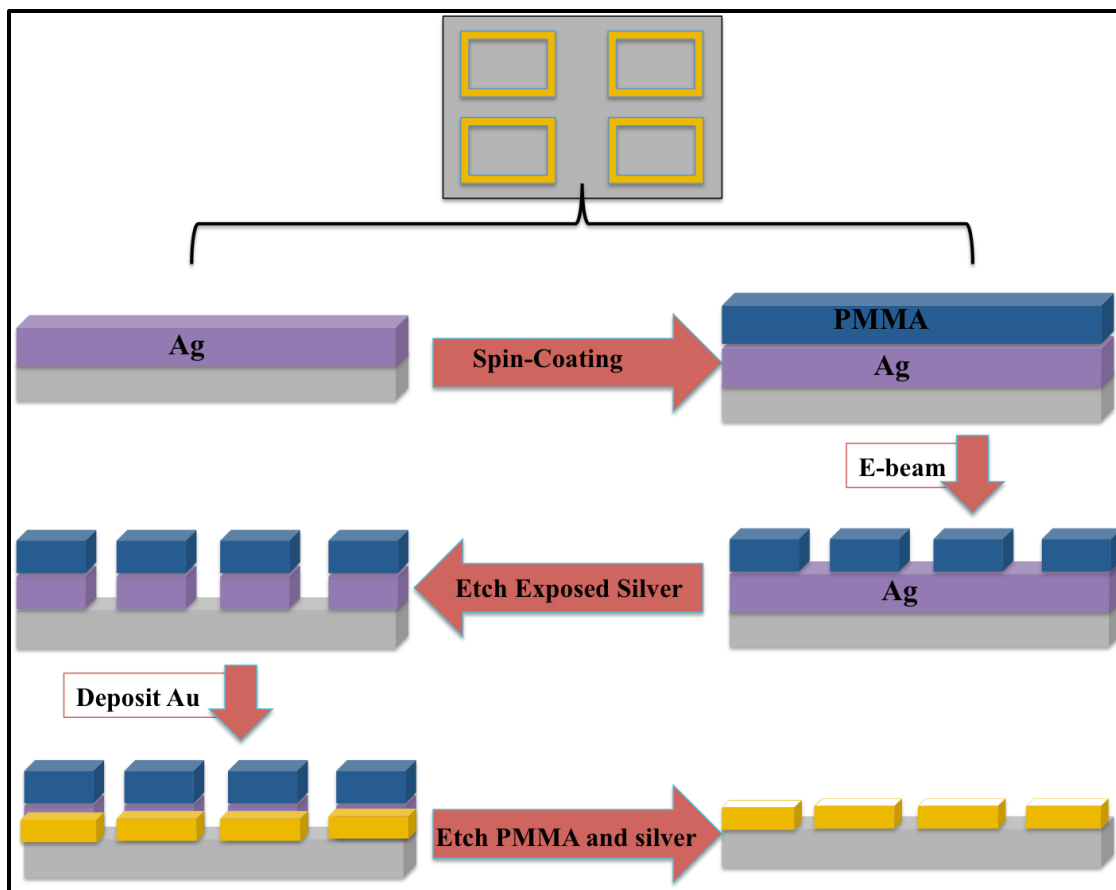
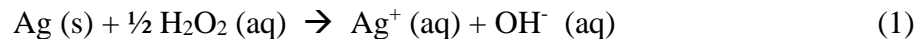


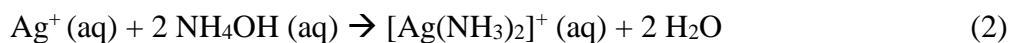
Figure 3. – Lithography sequence of bottom-up, top-down techniques for the patterning of nano-frames.

The high resolution PMMA photoresist is primarily used as a positive photoresist, meaning that when exposed to the e-beam, the polymer scissions into smaller and smaller fragments (with increased voltage and dwell time), which allows for those areas to be washed away much easier than the unexposed portion using the developer. Alternatively, at high enough dosage, PMMA can act as a negative photoresist, meaning the PMMA will polymerize even further, strengthening the exposed sections.¹⁸ Using PMMA to make samples of both negative and positive resists, we found that both tones can be used to obtain the desired silver pedestals; however, due to the high dwell time required for the negative tone, the negative tone required much more time to create the patterns, thus, the positive tone is preferred to create large arrays quickly and efficiently.

Chemically etching silver, by the 1:1 (by volume) addition of H₂O₂ and NH₄OH, uses H₂O₂ as an oxidation agent to oxidize Ag atoms, following the reaction in Eq. 1.

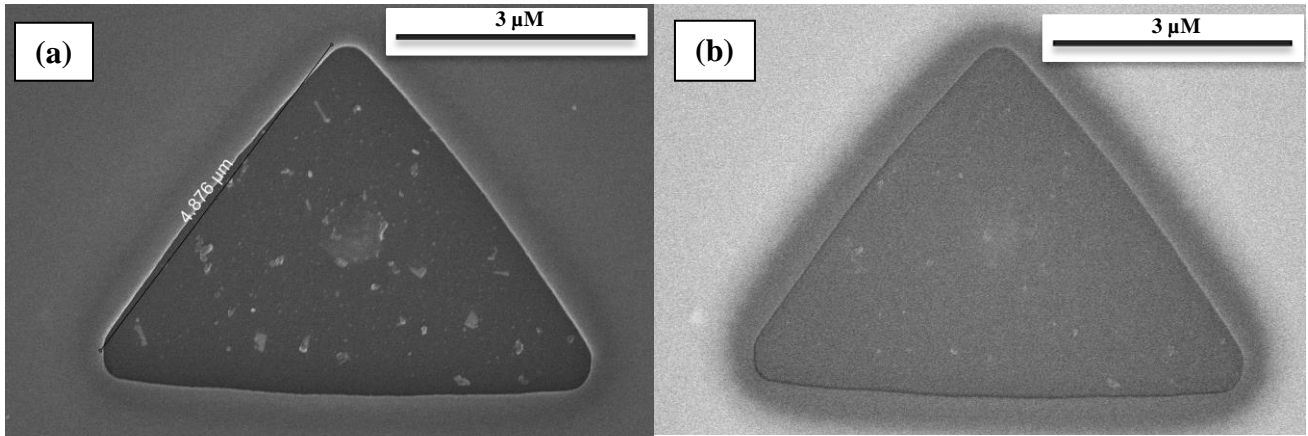


The NH₄OH works as a clean coordination agent to dissolve oxidized silver, following the reaction in Eq. 2.¹⁷



The rapid speed and violent etching of the silver made it difficult to control the extent to which the silver was removed. The silver was often etched beyond the exposed area, removing the surrounding silver which was still protected by PMMA. Figure 4a and b show the area where silver below the PMMA layer had been etched – the lighter areas on Figure 4b correspond to the PMMA and silver layers, while the darker region corresponds to the exposed glass substrate.

Figure 4. – (a) SEM image of undercutting after silver etching with the (b) backscattering image.



Furthermore, effects of the undercutting of the PMMA, due to receding silver, is observed by surface destruction caused during SEM imaging. The surface destruction shown in Fig. 5 is due to surface charging, a common problem with SEM imaging, resulting from electron trapping in insulators (i.e. the soda-lime glass substrate); although this is typically avoided by dispensing a thin-layer of AuPd (providing a conductive surface layer for the electrons), the AuPd was unable to coat the exposed glass in the undercut area of PMMA, thus, imaging the area results in high surface charging and eventual destruction of the silver and PMMA layers.

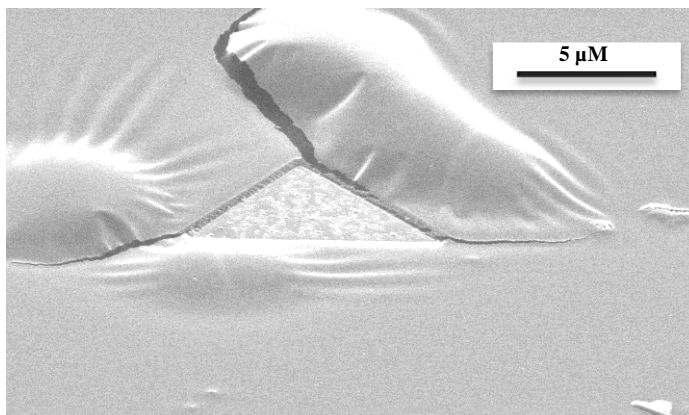


Figure 5. – SEM image of the damage caused by surface charging, showing the PMMA lifting off the substrate.

To ensure that silver had been removed from the triangle pits, an energy-dispersive X-ray spectroscopy (EDS) spectrum was taken for a spot within the triangle and outside of the triangle (where the presence of PMMA and silver is guaranteed). Figure 6 shows the two points chosen for EDS, one being within the triangle and the other, in an area where silver is expected.

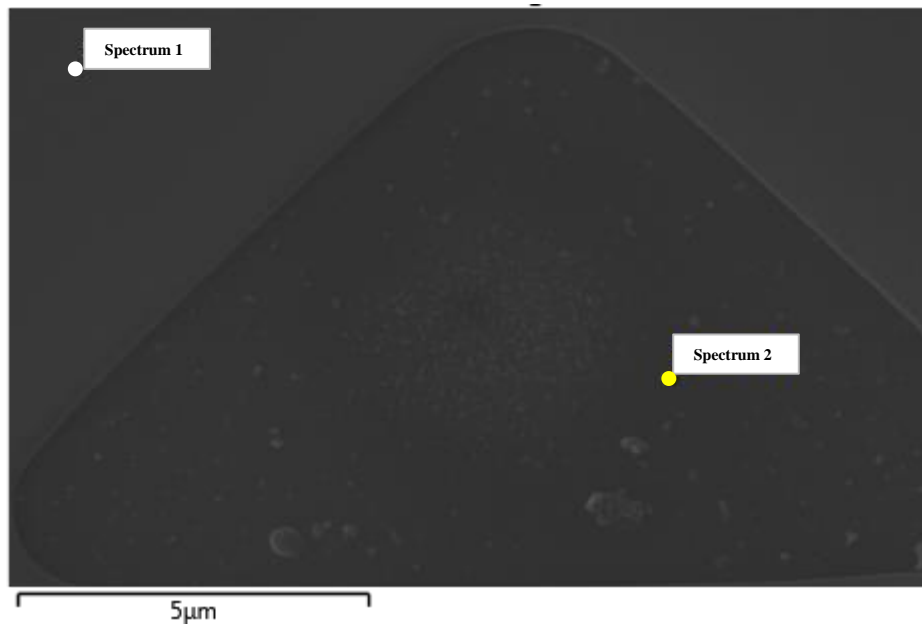


Figure 6. – SEM image of the areas chosen for EDS analysis, one being inside the triangle and the other outside.

Table 1 shows the results of the EDS – the spectrum taken within the triangle detects no carbon or silver, thus, it lacks both the PMMA and silver layers, respectively. Similarly, Spectrum1 detects both the PMMA and silver layers which have not been etched away.

Table 1. – EDS results of the points corresponding to the areas designated in Fig. 6.

| Spectrum Element | Spectrum 1 | Spectrum 2 |
|-------------------------|-------------------|-------------------|
| C | 61.44 | ----- |
| O | 13.46 | 52.14 |
| Na | 3.12 | 8.28 |
| Mg | 1 | 2.58 |
| Al | 0.3 | 0.52 |
| Si | 15.45 | 31.75 |
| K | 0.3 | 0.48 |
| Ca | 1.68 | 3.1 |
| Pd | 0.49 | 0.68 |
| Ag | 2.47 | ----- |
| Au | 0.28 | 0.46 |

Moving forward from these recent results, Au can be deposited after silver etching; however, when determining whether the deposition was successful via SEM and EDS, the AuPd layer required for SEM imaging would cause a false positive-like result from the EDS (Au of the AuPd layer would be detected regardless of where Au was deposited or not). Therefore, Pt is deposited instead, as it is easily detected by EDS. Once Pt has been successfully deposited, the remaining PMMA and silver can be removed, leading to the final nano-frames. We aim to reduce the size of the nano-frames, eventually obtaining a sub-100 nm size.

III. Conclusion

We are advancing an e-beam lithography technique able to make customized arrays of nanostructures. The photoresist PMMA was utilized because of its high resolution and ease of use. The optimal conditions for PMMA layering lead to a layer thickness of $\sim 1 \mu\text{m}$, which maintained sufficient structural integrity for development, silver etching, and Pt deposition. Determination of the ideal parameters for PMMA exposure using e-beam lithography have allowed for the fabrication of structures of varying complexity, with sub- $5 \mu\text{m}$ sizes, while maintaining the sharp edges and sides needed for the final nano-frames. Deposition of Pt or Au for the nano-frame structure was not yet achieved, but we aim to further advance our process to obtain the nano-frame structure, which will then be characterized to determine their optical and catalytic abilities.

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