Comparison of Au feature formation using two Au-calixarene resists, electron beam lithography, and low temperature organic removal

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Formation of positioned inorganic features have important applications in plasmonics, electronics, and catalysis. A flexible means to do so is through electron beam direct write (EBDW) of organo-metallic systems followed by pyrolysis, first demonstrated by Craighead and Schivone in a proprietary resist system.[1] More recently Corbiere *et. al.* wrote 2-dimensional arrays of nanoparticles using a Au(1) thiolate precursor to create nanoparticles.[2] Alternatively, authors have investigated EBDW to directly pattern nanoparticle-polymer films with Y. Chen, *et. al.* investigating the mechanism of e-beam induced sintering.[3]

Here we compare direct write of two Au bound calixarene resists—approximately the same average atomic number and organic/inorganic ratio, but different initial Au distribution (Figure 1). In the Au-1 system, there are two gold atoms bound to each calixarene (Fig. 1a) whereas in the Au-11 system, 5 calixarenes are bound to a cluster of 11 gold atoms (Fig. 1b). The Au-11 system offers a precursor type previously unexplored, where a sub-1 nm metal cluster is covalently bound to the organic. In addition, comparing the two systems allows us to better understand the role of molecular architecture.

Fig. 2a and 2b shows Au-1 and Au-11 systems after films are spun-on, e-beam exposed, and developed. The same line thickness is achieved in the Au-11 system at 4x less dose albeit with 3x higher line edge roughness. High voltage SEM reveals resolvable gold nanoparticles have formed in the Au-11 system (Fig. 2d) but are not visible in the Au-1 system (Fig. 2c). After oxygen plasma treatment, the volume of gold remaining (assuming spherical particles) in the Au-1 system (Fig. 3a), corresponds to ~ the initial volume of gold in the matrix. Significant organic residue is left in Au-11 system (Figure3b). The final size of the visible gold particles is determined by the post development line size, distance between neighboring features, oxygen treatment time, and the thickness of the resist. Increasing the film thickness increases the coverage of gold towards more continuous features yet with dense feature spacings, this comes at the expense of pattern collapse. Mechanisms of exposure and agglomeration will be discussed.

References:
1. H. G. Craighead and L. M. Schiavone, Appl. Phys. Lett. **48** (25), 1748-1750 (1986).
2. M. K. Corbierre, J. Beerens and R. B. Lennox, Chem. Mater. **17** (23), 5774-5779 (2005).
3. Y. Chen, R. E. Palmer and J. P. Wilcoxon, Langmuir **22** (6), 2851-2855 (2006).

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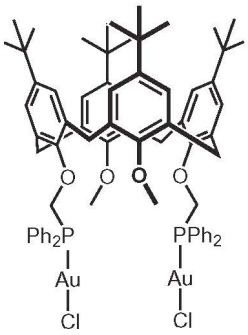
a



b

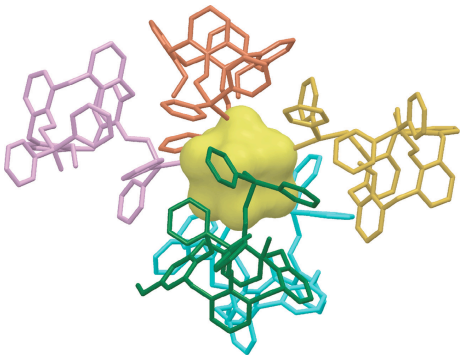


Figure 1: Two Au-calixarene systems are investigated, a Au(1)calixarene and a Au 11 cluster bound to 5 calixarenes. The calixarene molecule is the same in both cases.

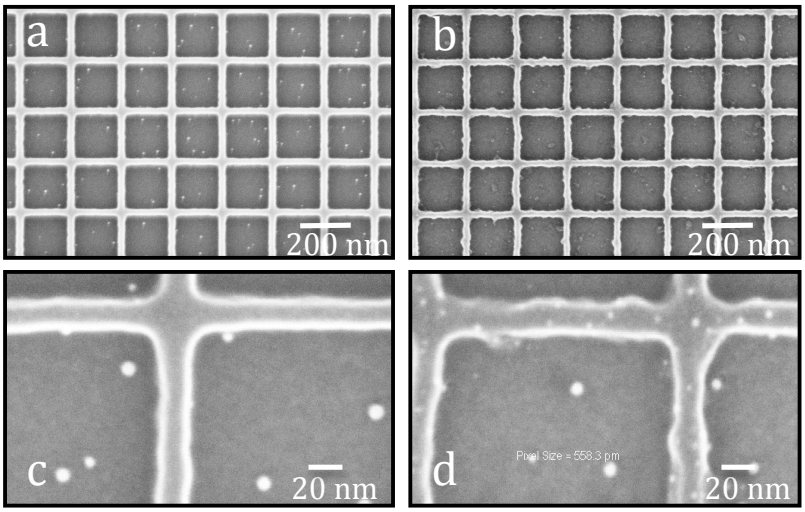


Figure 2: Comparison of exposed and developed lines in two calixarene systems. Dose to get the same final lines sizes is 4x higher in the Au-1 system (a) but the LER is higher in the Au-11 system (b). SEM images at 20kv do not resolve gold particles in the Au-1 (c) but are evident in the Au-11 lines.

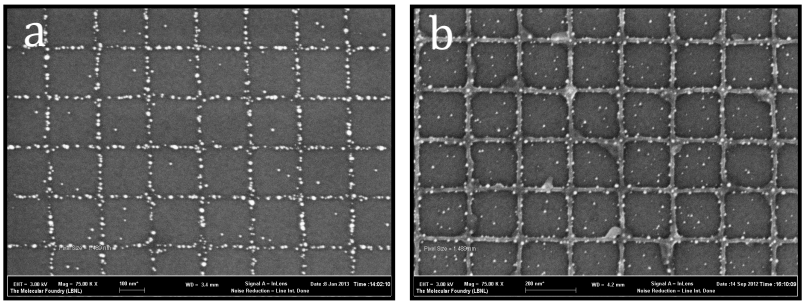


Figure 3: After the same oxygen plasma treatments, gold particles are clearly visible in the Au-1 (a) and Au-11 (b) systems but an organic residue remains in the Au-11 system. The lines are exposed at the same doses as those in Figure 2.