

Edge Spreading Lithography and Its Application to the Fabrication of Mesoscopic Gold and Silver Rings

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This paper describes a simple and convenient method that develops the outer profile of an object (serving as a physical guide) to generate mesoscopic structures such as rings on the surface of a solid substrate. This method exploits the reactive spreading of self-assembled monolayers (SAMs) on coinage metals,¹ which is supported by the diffusion of alkanethiols from a reservoir along the surface of a guide. We have demonstrated this concept by using (i) a flat poly(dimethyl siloxane) (PDMS) stamp inked with a solution of either octadecanethiol (ODT) or eicosanethiol (ECT) in ethanol; (ii) a two-dimensional (2D) array of spherical colloids as the guide; and (iii) a thin film of Au or Ag supported on a silicon wafer as the substrate to generate 2D arrays of Au or Ag rings. This particular approach combines the elements of microcontact printing (μ CP)² with nanosphere lithography,³ resulting in a novel variant of edge lithography. Edge lithography comprises an ensemble of techniques such as photolithography with phase-shifting masks,⁴ controlled undercutting,⁵ topographically directed etching,⁶ and others.⁷ These techniques utilize the edges of patterns to define the features of resultant structures; they contribute effectively to size-reduction, and provide attractive routes for generating high-resolution wires, trenches, and other related structures. Our approach is set apart from preceding techniques by the way we generate the templates and by the flexibility of the actual patterning process. In the following, we refer to this approach as edge spreading lithography, or ESL.

Figure 1 outlines the procedure for ESL, which begins with the assembly of silica beads on the surface of a thin Au or Ag film.⁸ We selected silica beads for a number of reasons: (i) they are inert to most organic solvents; (ii) they are commercially available as monodispersed samples in a range of sizes; (iii) they can be readily assembled into ordered arrays over large areas;^{8,9} (iv) they are mechanically more robust than most polymer beads of equivalent size; and (v) their hydrophilic surfaces support the spreading of the thiols. Typically, a planar PDMS stamp is inked with an ethanol solution of thiol, dried, and placed on a 2D array of beads. The stamp serves as an ink reservoir, from which molecules are released during contact. These molecules are guided along the surface of each bead to the substrate where they form a SAM, whose area can expand laterally via reactive spreading as long as a continuous supply of thiol is maintained.¹ The circular footprint (d) of each bead thereby dictates the shape of the emerging pattern: it determines the region that is inaccessible to thiol molecules, and its circular symmetry propagates through the lateral spreading of the SAM. Upon removal of the stamp and lift-off of the beads, the ring pattern is developed by wet etching with aqueous Fe^{3+} /thiourea using the patterned SAM as a resist.¹⁰

Figure 2 shows several examples of arrayed Au rings fabricated using ESL.¹¹ It was possible to transfer a self-assembled lattice of beads into the corresponding ring pattern over a large area, at a high yield, and with good uniformity. Figure 2A shows the SEM image of a small portion taken from a single domain of $\sim 50 \mu\text{m}$

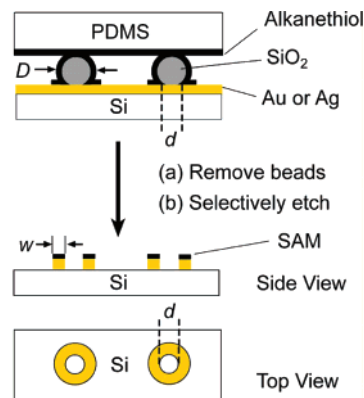


Figure 1. Schematic illustration of ESL. Arrayed silica beads are used to direct the transport of alkanethiols from a planar PDMS stamp onto the surface of a coinage metal film. Upon reaching the metal surface, the thiol molecules self-assemble into a monolayer, which is confined by the footprint (d) of each bead and the lateral spreading (w) of the thiols. Once the beads have been removed, the unprotected regions of the metal can be selectively dissolved in a wet etching process.

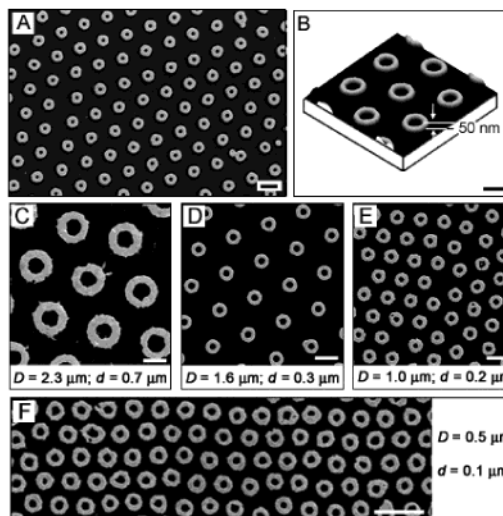


Figure 2. Ring patterns fabricated by ESL with arrays of silica beads deposited on Au films of 50 nm in thickness. The patterned arrays can have high uniformity as shown by the SEM image in (A). The AFM image in (B) illustrates the excellent lithographic definition that can be achieved. The SEM images in (C–F) illustrate the trends that could be observed when silica beads of various sizes were used. Although the initial lattice was preserved in each sample, the footprints showed some variations that were possibly caused by the difference in the interaction between individual beads with the gold surface. All scale bars are $1 \mu\text{m}$.

by $\sim 75 \mu\text{m}$ in area. The rings are characterized by high contrast and fine-edge resolution; their three-dimensional profile is shown by the atomic force microscopy (AFM) image (Figure 2B). The lattice constant of the arrayed rings and the inner diameter of each

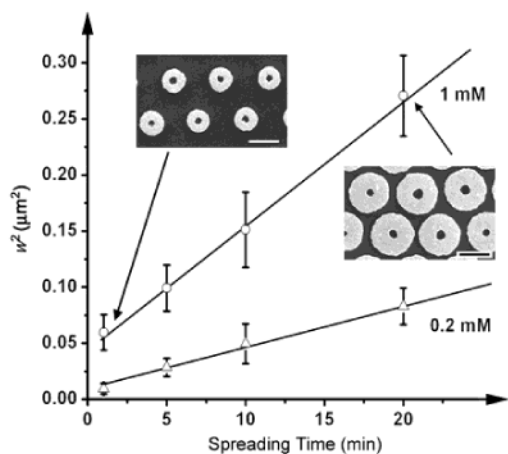


Figure 3. The width of the rings could be conveniently controlled by two parameters: the concentration of thiol in the ink and the spreading time. Each set of data was obtained by inking planar PDMS stamps with a solution of either 0.2 (triangles) or 1.0 mM (circles) ODT in ethanol and leaving them in contact with 2D arrays of silica beads ($D = 1.6 \mu\text{m}$) supported on Ag films ($\sim 50 \text{ nm}$ in thickness) for different periods of time. The SEM images illustrate two typical examples in which the rings were 240 and 520 nm in width, respectively. The scale bars are $1 \mu\text{m}$.

ring can be varied by changing the size of the silica beads (Figure 2C–F). The spacing between the beads was reproduced in a 1:1 ratio in the array of rings. For example, when the diameter of the beads was reduced from 2.3 to $0.5 \mu\text{m}$, the spacing in the corresponding array of rings decreased accordingly. The correlation between the diameter (D) of the beads and the inner diameter (d) of the rings is less pronounced but was found to follow the same general trend for beads with D between 2.3 and $0.5 \mu\text{m}$. For beads in this size range, the value of d was on the order of 20–30% of D . It is, however, difficult to directly compare d for beads with different diameters due to possible differences in their mechanical properties, the surfactants present in the colloidal suspension, and printing artifacts. We also observed notable exceptions from these values at the edges of arrays where the beads are prone to motion upon contact with the PDMS stamp. We probed the limit of this approach by reducing the bead diameter to 150 nm (data not shown). These experiments did not yield well-defined ring patterns mainly because the diffusion zones of the SAMs readily overlapped at these small scales, underlining the need for better control over the diffusion process.

The plots in Figure 3 show the evolution of the ring width (w) as a function of time during which the PDMS stamp was kept in contact with the beads. In this case, silica beads were assembled on thin films of Ag and used to direct the delivery of ODT molecules from PDMS stamps that were inked with either 0.2 or 1.0 mM solutions of this thiol in ethanol. For both concentrations, the graph reveals a linear relationship between w^2 and the spreading time within a period of 1–20 min.¹² When the stamp was placed on the arrayed beads for a shorter period of time (e.g., 30 s), the SAM was unable to adequately protect the Ag surface against etching, indicating that not enough molecules had reached the surface. The data also suggests the appearance of an onset width that is related to the ODT concentration. This finding implies that the diffusion front along the surface of each bead is fluidlike, and it is primarily composed of ODT molecules. Similar trends were also observed by using Au substrates, by exchanging ODT for ECT, or by switching to a range of other concentrations.

In summary, we have established a new strategy for fabricating mesoscopic Au and Ag rings rapidly and inexpensively by controlling the reactive spreading of thiols from the edges of arrayed

silica beads. While the size of the beads had a direct influence on the spacing between the rings and their inner diameters, control of the spreading process was key to tuning the widths of resultant metal rings. Although arrayed rings could be formed over large areas and in parallel using this approach, the method remains sensitive to the defects, distortions, and domain boundaries inherent to 2D lattices of spherical colloids. These limitations might be less important when these metal structures are used for surface-enhanced Raman spectroscopy (SERS)^{13,14} or when they are released from the substrate for further use (e.g., as building blocks in self-assembly¹⁵). While silica beads served as a convenient model system for these demonstrations, we feel that structures other than circular rings might be obtained with this technique by using objects with different footprints.

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Supporting Information Available: Experimental methods and materials and an SEM image of free-standing gold rings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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