

Scanning Electron Microscopy Evaluation of Soft-lithography Techniques

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Soft-lithography techniques have been developed to create surfaces with chemical patterns for such diverse fields as biosensing and molecular electronics. Microcontact printing (μ CP) is the most widely used soft-lithography method to create chemically patterned surfaces.¹ We have utilized a scanning electron microscope (SEM) to characterize chemical patterns prepared by μ CP, and three recently developed chemical patterning techniques that enhance the sophistication and resolution of soft lithography – microdisplacement printing (μ DP),² microcontact insertion printing (μ CIP),³ and lithography-assisted chemical patterning.⁴

One of the limitations of μ CP is the tendency of the ink molecules to spread across the surface (Fig. 1). Microdisplacement printing circumvents this by utilizing a preassembled, labile self-assembled monolayer (SAM) of 1-adamantanethiol (AD) on the surface. The AD SAM is selectively displaced by the more strongly bound ink molecule from the raised regions of a patterned elastomeric stamp and simultaneously prevents the lateral diffusion of the ink molecule. This improves the fidelity of chemical patterns created by μ DP (Fig. 2).² Microcontact insertion printing is a new technique for the creation of chemical patterns of inserted molecules at dilute coverages ($\leq 10\%$). This insertion places the ink molecule in defects of the host SAM only in the raised regions of an elastomeric stamp (Fig. 3). The surface concentration of inserted molecules can be controlled based on the stamping time and concentration of the ink molecule.³ Lithography-assisted chemical patterning utilizes a robust lithographic resist (LOR) that is capable of withstanding self-assembly deposition conditions to create high-quality chemical patterns (Fig. 4). The ability to pattern chemical functionalities without intercalation and parallel processing are some of the unique advantages of this technique.⁴ Additionally, the SEM contrast observed in chemical patterns has been attributed to differences in secondary electron scattering and surface potentials. Here, we describe how the operating voltage also determines the relative contrasts observed in the SEM images of chemical patterns.

¹ Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.* **37**, 551 (1998).

² A. A. Dameron, J. R. Hampton, R. K. Smith, T. J. Mullen, S. D. Gillmor, and P. S. Weiss, *Nano Lett.* **5**, 1834 (2005).

³ M. E. Anderson, C. Srinivasan, J. N. Hohman, E. M. Carter, M. W. Horn, and P. S. Weiss, *Adv. Mater.* **18**, 3258 (2006).

⁴ T. J. Mullen, C. Srinivasan, J. N. Hohman, S. D. Gillmor, M. J. Shuster, M. W. Horn, A. M. Andrews, and P. S. Weiss, *Appl. Phys. Lett.* (2007), in press.

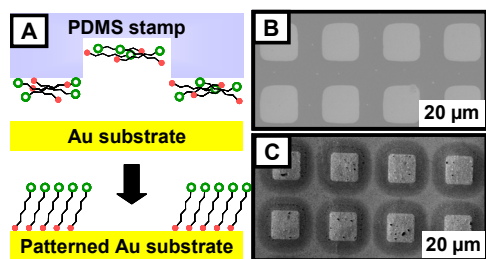


Fig. 1: Micromaterial printing (μ CP):* (a) Schematic representation of μ CP with alkanethiolate monolayers on Au. A molecularly-inked elastomeric stamp with patterned relief features is brought in contact with an Au substrate resulting in the transfer of the ink molecule from the stamp onto the substrate in the raised regions of the elastomeric stamp. (b) Chemical pattern of an *n*-octadecanethiolate SAM on Au. (c) Chemical pattern of an 11-mercaptoundecanoic acid SAM on Au. The lower intermolecular interactions between the SAM molecules result in lateral diffusion and cause a “halo” to appear surrounding the chemical pattern in the SEM image.

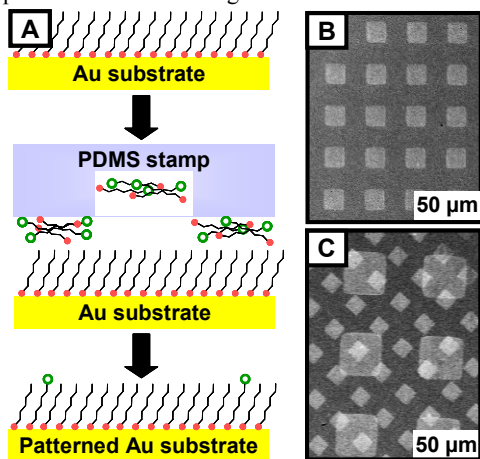


Fig. 3: Microcontact insertion printing (μ CIP):* (a) Schematic representation of μ CIP with alkanethiolate monolayers on Au. A molecularly-inked elastomeric stamp with patterned relief features is brought in contact with an Au substrate containing a preassembled SAM of *n*-octanethiol (C8) resulting in the insertion of the ink molecule into the host SAM from raised regions of the elastomeric stamp. (b) A μ CIP pattern of an 11-mercaptoundecanoic acid SAM (brighter areas) inserted into a C8 SAM on Au and stamped for ~30 min. (c) A double μ CIP pattern of a 11-mercaptoundecanoic acid SAM inserted into a C8 SAM on Au using 25 μ m and 10 μ m stamps for 30 min each. The increase in contrast in the overpatterned regions is due to the larger concentration of inserted molecules. The concentration of inserted molecules can be controlled based on the ink concentration and the stamping time.

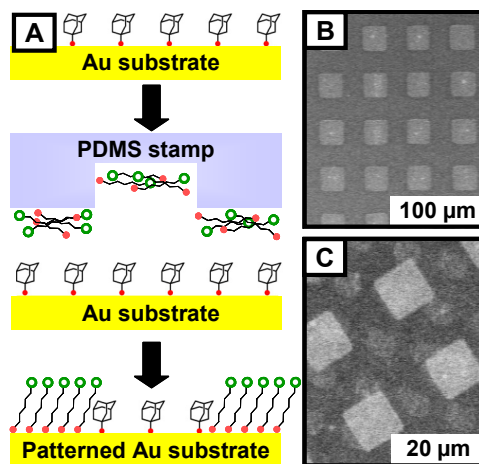


Fig. 2: Microdisplacement printing (μ DP):* (a) Schematic representation of μ DP with alkanethiolate monolayers on Au. A molecularly-inked elastomeric stamp with patterned relief features is brought in contact with a Au substrate containing a preassembled SAM of 1-adamantanethiol (AD) resulting in the displacement of the AD SAM by the ink molecule from raised regions of the elastomeric stamp. (b) A μ DP pattern of an 11-mercaptoundecanoic acid SAM (brighter areas) on Au. The resulting chemical pattern does not contain the “halo” seen in Fig. 1 (c). (c) A double μ DP pattern of an 11-mercaptoundecanoic acid (10 μ m brighter areas) and *n*-dodecanethiolate (5 μ m brighter areas) on Au.

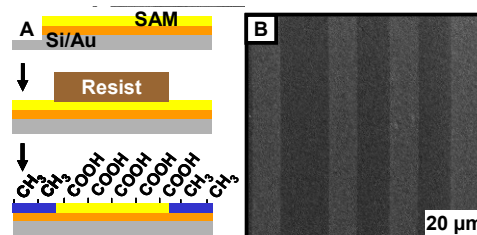


Fig. 4: Lithography-assisted chemical patterning:* (a) Schematic representation of lithography-assisted chemical patterning of alkanethiolate monolayers on Au that utilizes a robust lithographic resist (LOR) that is capable of withstanding self-assembly deposition conditions to create high-quality chemical patterns. The first SAM is deposited on the surface, a photopattern is transferred to the LOR, the first SAM is removed from the exposed patterns of the LOR by photooxidation, the second SAM is codeposited on the surface while the LOR protects the first SAM below it, and finally the LOR is removed. (b) A chemical pattern of a 16-mercaptohexadecanoic acid SAM (darker areas) and *n*-octadecanethiol SAM (brighter areas).

*All images correspond to field-emission scanning electron microscopy images acquired at operating voltages of 1 keV (Fig. 1-3) and 5 keV (Fig. 4).