Patterning Materials at the One Nanometer Length Scale with an Electron Beam

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Although patterning materials at ever-higher resolution has long been an engine that fuels new technologies, designing materials at the one nanometer length scale still remains in the realm of chemical synthesis.[1, 2] Although electron-beam lithography (EBL) has been the principal patterning method to fabricate arbitrary-shaped sub-50 nanometer structures, it has not reliably provided sub-4 nanometer patterns, except under specialized conditions such as with assist structures,[3] and using long-exposure of self-developing resists.[4] Nanopatterning techniques that can surpass the 4 nanometer resolution limit, such as electron-beam induced deposition,[5] or scanning probe lithography[6] require orders-of-magnitude longer exposure time than EBL. Finally, transferring patterns from the resist to a material at the sub-4 nanometers length scale remains a challenge.[7] In this work, we employed an aberration-corrected scanning transmission electron microscope augmented with a pattern generator for lithography using 200 keV electrons and 1 Å spot size to achieve unprecedented resolution.

Here we show aberration-corrected EBL at the one nanometer length scale using widely available resist poly(methyl methacrylate) (PMMA), and we show successful pattern transfer to semiconductor and metallic materials at the sub-5 nanometer scale. We show feature sizes of 1.7 ± 0.5 nm and pattern periodicity of 10.7 nm for negative-tone PMMA, and feature sizes of 2.5 ± 0.7 nm and periodicity of 17.5 nm for positive-tone PMMA (Figure 1). These results are the smallest and highest density patterns in PMMA and the smallest isolated feature achieved in any conventional resist. These patterning results indicate that polymer-based nanofabrication can achieve features sizes comparable to the Kuhn length of PMMA and more than ten times smaller than its radius of gyration. Furthermore, we showed transfer of the resist patterns to AuPd and ZnO, demonstrating the general applicability of this technique (Figure 2). As evidence, we show AuPd dot patterns with 1 to 3 nm diameter (Fig. 2b), nanowires with 6 nm linewidth (Fig. 2c), and nano-gaps down to 6 nm. In addition, we fabricated ZnO nano-dots with 2.8 nm average diameter (Fig. 2d-e). We will perform additional pattern transfer by reactive ion etching and characterize the electronic and optical properties of materials at the sub-5 nm length scale. We expect that aberration-corrected EBL will increase the resolution, speed, and complexity in sub-5 nm nanomaterial fabrication.

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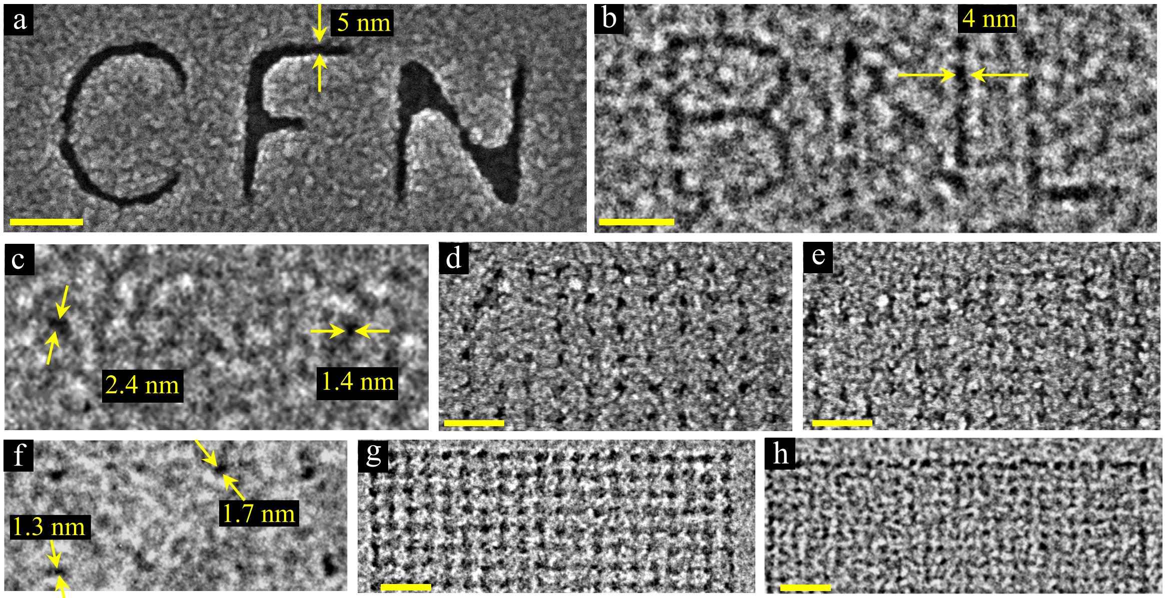

Figure. 1. Aberration-corrected electron-beam lithography in PMMA on top of 5-nm-thick SiN_x membrane. (**a**) Scanning electron micrograph (SEM) of arbitrary patterns in positive-tone PMMA. The PMMA was coated with 5 nm of Ti and 10 nm of Au for all subsequent positive tone PMMA patterns. (**b**) TEM micrograph of arbitrary patterns in negative-tone PMMA. (**c**) SEM images of the smallest patterned holes in positive-tone PMMA, with average hole diameter of 2.5 ± 0.7nm. (**d**) and (**e**) SEM images of PMMA hole arrays of 21.5 and 17.5 nm pitch, respectively. (**f**) TEM micrograph of pillar arrays in negative-tone PMMA with 20 nm pitch. The average pillar diameter was 1.7 ± 0.5 nm. (**g**) and (**h**) TEM micrographs of negative-tone PMMA pillar arrays of 15.2 and 10.7 nm pitch, respectively. All scale bars are 40 nm.

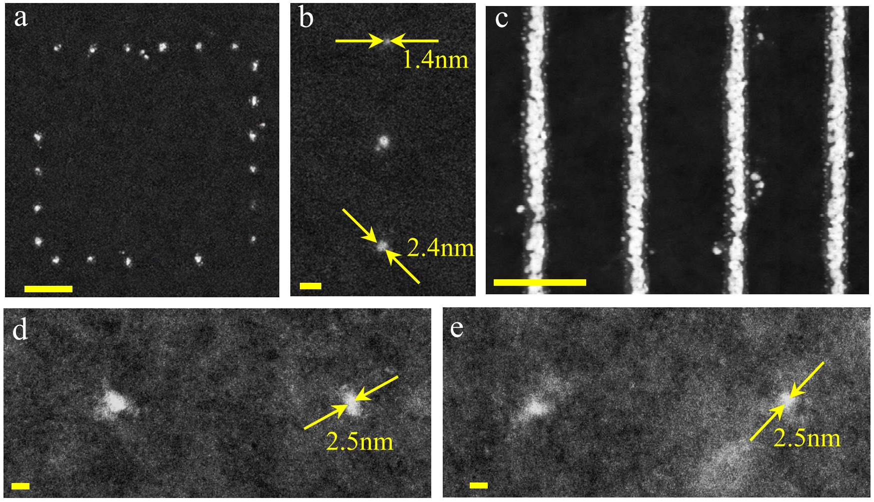

Figure. 2. Pattern transfer to AuPd and ZnO. All micrographs are STEM images in ADF mode. (**a**)-(**c**) Nanostructures fabricated with positive-tone PMMA patterning and lift-off, consisting of 13-nm-thick AuPd on top of 3-nm-thick Ti on 5-nm-thick SiN_x membrane. (**a**) AuPd/Ti dotted frame designed with 30 nm pitch. (**b**) Magnified view of the smallest dot array with dot diameters from 1 to 3 nm. (**c**) Narrowest fabricated wires that were continuous with 6 nm linewidth. (**d**)-(**e**) Nanostructures fabricated by sequential synthesis infiltration (i.e., ALD-based vapor-phase infiltration of diethylzinc into the cross-linked PMMA resist, followed by conversion to ZnO by reaction with water vapor and polymer removal by oxygen plasma) in negative-tone PMMA, resulting in ZnO nanostructures on SiN_x membrane. The ZnO dot array have average diameter of 2.8 ± 0.9 nm. The scale bars of (**a**) and (**c**) are 40 nm and the others are 5 nm.