Electron-Beam Induced Deposition using Liquid-Phase Precursors

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Focused electron-beam induced deposition (EBID) and etching (EBIE) allow the direct formation of metal and dielectric nanostructures using gaseous reactants. These processes have been widely investigated for nanoscale device prototyping and for lithographic mask repair.[1] However, focused electron-beam induced processes using liquid-phase reactants remain almost entirely unexplored and unexploited. Use of liquid phase reactants would provide new deposition mechanisms, allow processing of new materials, provide a wider variety of precursors, and reduce problems with contamination and substrate charging. Here we report direct electron-beam induced deposition of 50-nm structures from a chloroplatinic acid (H_2PtCl_6) solution. To our knowledge this is the first demonstration of e-beam induced deposition from a true liquid precursor.

As shown in Fig. 1, depositions were carried out in QuantomiX QX-102 WETSEM capsules which separate a liquid from the vacuum chamber using a thin (~150nm) polyimide membrane.[2] Two of these capsules were filled with a 1% by weight solution of H_2PtCl_6 in deionized water. A third capsule, serving as a control, was filled with the QuantomiX imaging buffer solution. Single pixel dots and lines were exposed at varying doses using a primary beam energy of 20keV in a Raith E-line electron-beam lithography tool. In the chloroplatinic acid filled capsules, ~50-nm diameter dots were deposited for point doses of 18pC and ~50-nm wide lines were deposited with a linear dose of 2.4μC/cm. In addition, some arbitrary patterns, such as four-point probe structures, were exposed. No deposition was observed in the control capsule even at doses up to 50 times higher than the required dose for the H_2PtCl_6 solution.

Electron micrographs were taken *in-situ*, i.e. through the membrane, during patterning. After patterning, the capsules were opened, the H_2PtCl_6 solution was aspirated, and the membranes were flushed 10 times with deionized water to remove any residual H_2PtCl_6. After drying, electron micrographs were taken of the underside of the membrane (the side formerly in contact with the H_2PtCl_6 solution) and the deposited patterns were imaged. These images confirm that deposition occurred on the underside of the membrane in contact with the solution. Both *in-situ* and *ex-situ* micrographs are shown in Fig. 2 and Fig. 3. Experiments are underway to determine the exact composition of the nanostructures; however, their high contrast and stability during SEM imaging, along with the lack of deposition in the control capsule, suggest that they consist of platinum or a platinum containing compound.

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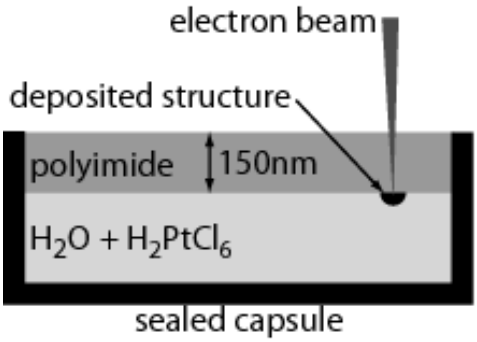
1 S. J. Randolph, J. D. Fowlkes, and P. D. Rack, Critical Reviews in Solid State and Materials Sciences **31**, 55 (2006).

2 S. Thiberge, O. Zik, and E. Moses, Review of Scientific Instruments **75**, 2280 (2004).

Fig. 1. Schematic of electron-beam induced deposition from a liquid precursor. A sealed capsule with a polyimide membrane separates the precursor solution from the lithography system's vacuum chamber. The membrane is electron transparent and allows both patterning and *in-situ* imaging. Here we used a 1% H_2PtCl_6 aqueous solution and a 20keV electron beam to deposit nanostructures at the membrane solution interface.



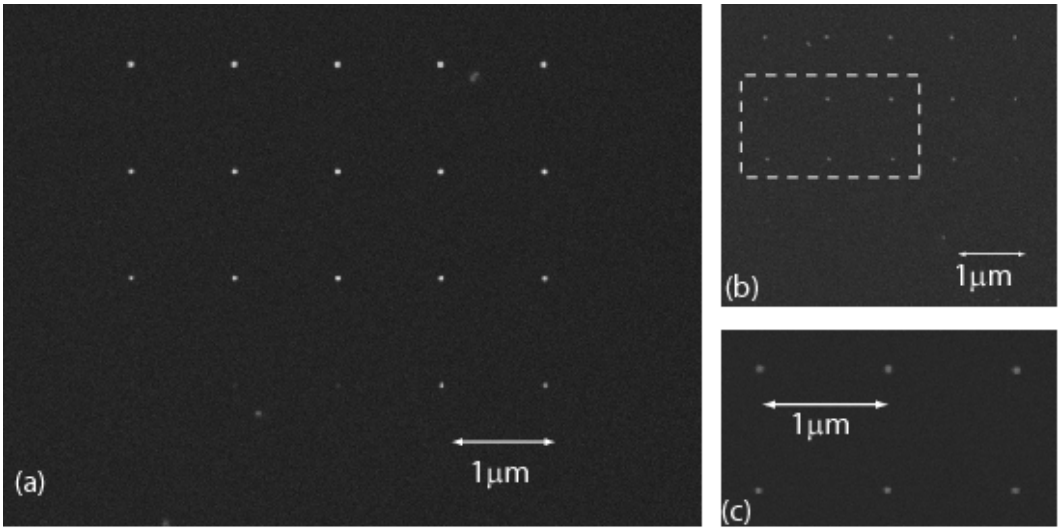


Fig. 2. Deposited nanostructures of ~50nm diameter using single pixel exposures. (a) *In-situ*, through the membrane, image of 5x4 pixel dose array. Doses range from 12pC (lower left, barely visible) to 51pC (upper right). (b) Image of same dot array imaged on the underside of the membrane after rinsing and drying. Image is reversed left to right because the membrane is inverted when imaging the underside. (c) Enlarged view of region indicated in (b).

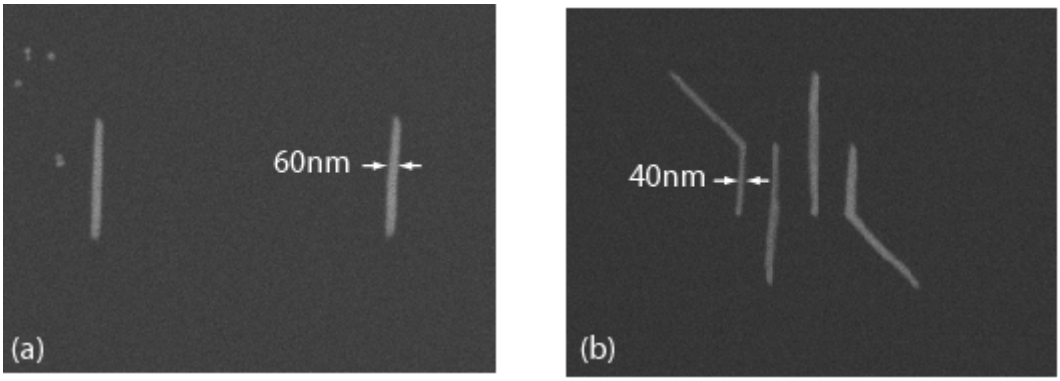


Fig. 3. E-beam induced deposition using single pixel wide lines. (a) Two lines exposed at linear doses of 2.5 and 2.6 μC/cm from left to right. (b) Four point measurement structure exposed with a dose of 2.4μC/cm. Both images were acquired from the underside of the membrane after rinsing and drying.