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Automated and Shaped-Controlled Liquid STEM Nanolithography

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There is a range of scanning probe and electron beam nanolithography platforms currently available for producing nano-scaled structures with complex shapes and chemistries from solid or gaseous phase precursors [1-2]. Recent studies have shown that the same concept can be applied to liquid phase precursors using liquid cells and electron beams with manual manipulation [3-4]. In the present work, an automated electron beam control system has been developed to precisely control the position and residence time of the STEM probe from a C_s aberration-corrected FEI Titan STEM operating at 300kV. The position of the STEM probe is controlled by applying bias waveforms to the X- and Y- STEM scan coils such that the focused STEM probe can be positioned in the X-Y plane either in a fixed position with a pre-defined dwell time or rastered in the X-Y plane with a variable translational velocity.

This system has been used for nanolithographic patterning of nm-scale 3D structures from liquid phase precursor solutions. An *in situ* liquid cell TEM holder was used to encapsulate a 10 μM H_2PdCl_4 aqueous solution between two 50 nm thick silicon nitride membranes. Radiolysis occurs when the electron beam interacts with the solution, forming complex radical species [5]. As a result, aqueous electrons (e_{aq}^-) are generated in the liquid, which effectively act as a reducing agent to reduce metallic Pd from the H_2PdCl_4 complex [6]. Thus, the principals of radiation chemistry within closed liquid cells combined with automated electron beam control can be exploited to nanolithographically-pattern structures of metallic Pd.

The Institute of Functional Imaging of Materials (IFIM) acronym was used to demonstrate the concept of liquid STEM nanolithography. The focused STEM probe was rastered through the liquid cell containing the 10 μM H_2PdCl_4 growth solution and Pd metal was reduced forming Pd nanocrystals directly onto the silicon nitride membrane and within the liquid cell through a nucleation and growth mechanism. An annular dark field (ADF) STEM image of the patterned "IFIM" text is shown in Figure 1a. As a result of chemically sensitive ADF STEM imaging, whereby intensity is proportional to the atomic number and thickness, the nanolithographically patterned Pd has a higher intensity when compared against the lower atomic number background of the silicon nitride membranes and the H_2PdCl_4 growth solution and therefore the electron beam reduced Pd structures can readily be characterized following patterning. It is clear by the size-scale and legibility of the IFIM letters shown in Figure 1a, that the nanolithography technique can be used to precisely control the position of the STEM probe and resultant Pd crystal deposition. Corresponding higher magnification images shown in Figures 1b-d, reveal that the pattern is composed of Pd nanocrystals having individual crystal sizes on the order of tens of nanometers with the exception of a few larger crystals (Figure 1b). It is interesting to note that the Pd nanocrystals are primarily confined within the local irradiated region of the IFIM pattern, e.g., there is limited nucleation and growth of Pd outside of this area. For liquid STEM nanolithography, precision-controlled nanosculpting is

governed by the interplay between electron dose, electron beam exposure time, diffusivity of e_{aq}^-, and nucleation and growth kinetics of the electron beam deposited crystals [7].

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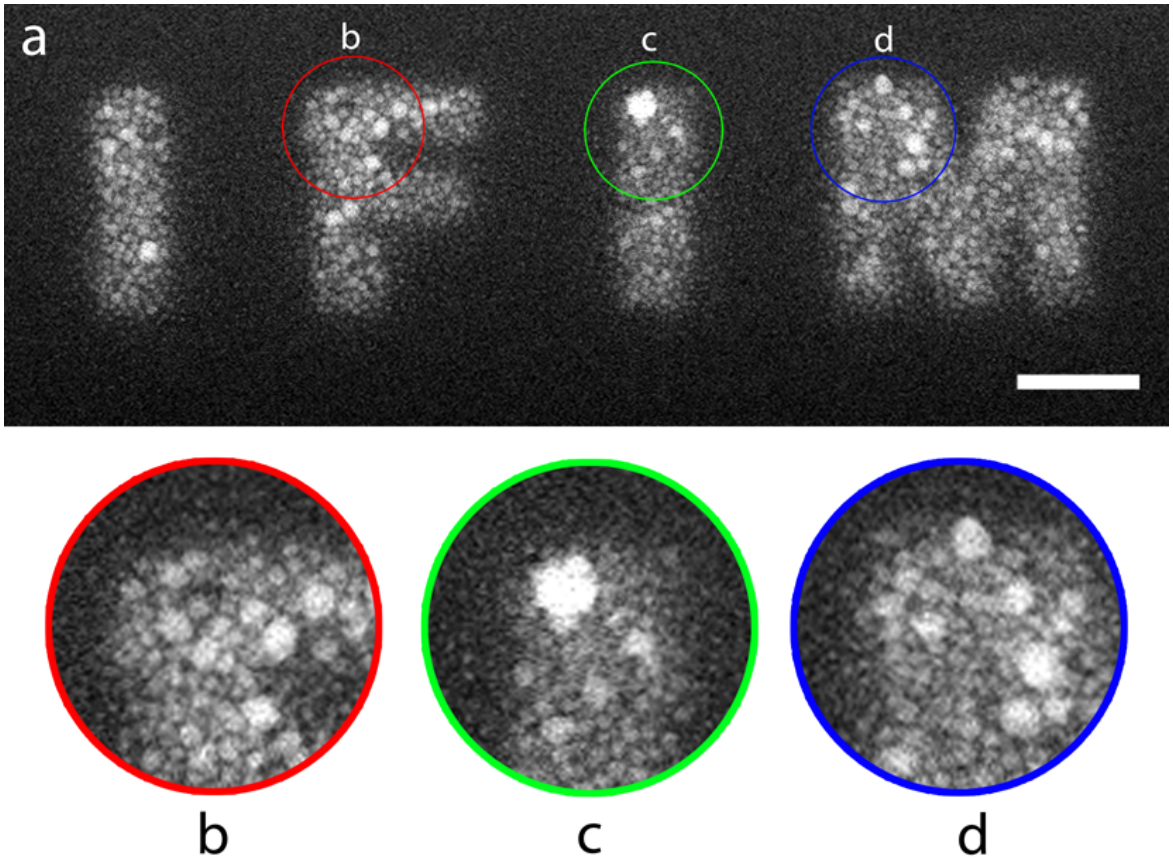

Figure 1. a) ADF STEM image showing the "IFIM" text nanolithographically patterned within a STEM liquid cell using a 10 μM H_2PdCl_4 precursor growth solution. Scale bar is 500 nm. b-d) Higher magnification ADF STEM images from several regions of the pattern showing the detailed nanocrystalline nature of the deposited Pd.

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