

Focused Electron-Beam-Induced Deposition of Platinum and Gold Nanostructures from Aqueous Solutions

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Focused electron-beam-induced deposition (EBID) from gaseous precursors has been studied at great length in recent years and proven viable for direct-write patterning of nanostructures.¹ Here we report on our progress in further developing LP-EBID, a still-nascent modality of the technique using bulk liquid precursors (LP) depicted in Fig. 1.^{2,3} LP-EBID promises a number of advantages over gas-phase EBID: enhanced purity and growth rate of the deposits; mitigation of proximity effects and substrate charging; and more benign, stable, and cost-effective precursors. In this report on LP-EBID, we describe how particle size varies with the charge dose and demonstrate the highest resolution we have achieved to date. In addition, we compare platinum and gold deposits obtained from different liquid precursors.

The dependence of the lateral size of platinum nanoparticles (Pt NPs) (Fig. 2(a)) follows a trend similar to that encountered in gas-phase EBID. As e-beam dose increases, rapid initial growth is followed by a more gradual increase in size and eventual saturation (Fig. 2(b), lower panel). A threshold dose of about 5pC per NP was required to initiate the deposition of Pt (Fig. 2(b), upper panel) from aqueous chloroplatinic acid (H_2PtCl_6) solutions. For some of the Pt NPs we also observed weak proximity effects, but these only became evident at doses 25 times the threshold dose. Regarding the resolution of LP-EBID, we have deposited Pt NPs of ~25nm-diameter in arrays of 60nm pitch (Fig. 2(c)) and 25nm-wide parallel lines also separated by 60nm (not shown).³ The resolution appears to be limited by pattern distortion due to proximity effects and/or to membrane distortion.

Following a process similar to that for Pt, gold (Au) can be deposited using liquid precursors containing chloraurate ions (AuCl_4^-). Deposition from a chloroauric acid solution (HAuCl_4) at a concentration similar to the Pt solution showed an onset of deposition at a dose of 1pC. As seen in Fig. 3(a), however, gold deposition of an array of dots produced inconsistent structures using this precursor and there was also evidence of membrane damage. A neutral Au precursor (NaAuCl_4) was found to yield more consistent deposits as shown in Fig. 3(c). However, a larger threshold dose of 15pC was required for the neutral solution of the same concentration. In both cases, the existence of “collateral deposition” (Fig. 4(a,b)) around the patterned area led to a less desirable result than in the case of Pt (Fig. 2).

EBID of both Pt and Au is possible using bulk liquid precursors containing chloroplatinate and chloraurate ions, respectively. Deposition of Pt from chloroplatinic acid produces uniform, 25nm structures with minimal collateral deposition. Deposition of Au from acidic and neutral chloraurate solutions also yields nanoscale structures, but with additional collateral deposition. Neutral gold solutions were found to produce more uniform deposits than acidic gold solutions. Finally, varying the precursor concentration has noticeable effects on threshold dose, deposit structure, and collateral deposition.

¹ W. F. van Dorp and C. W. Hagen, *J. Appl. Phys.* **104**, 081301 (2008).

² E. U. Donev and J. T. Hastings, *Nano Lett.* **9**, 2715 (2009).

³ E. U. Donev and J. T. Hastings, *Nanotechnology* **20**, 505302 (2009).

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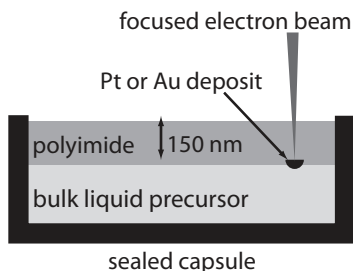


Fig. 1. Schematic of liquid-precursor electron-beam-induced deposition (LP-EBID) of platinum or gold from aqueous solutions of chloroplatinic acid (H_2PtCl_6) or chloroauric acid (HAuCl_4), respectively. The solution is separated from the vacuum chamber by a polyimide membrane and the electron beam deposits nanostructures at the membrane–solution interface.

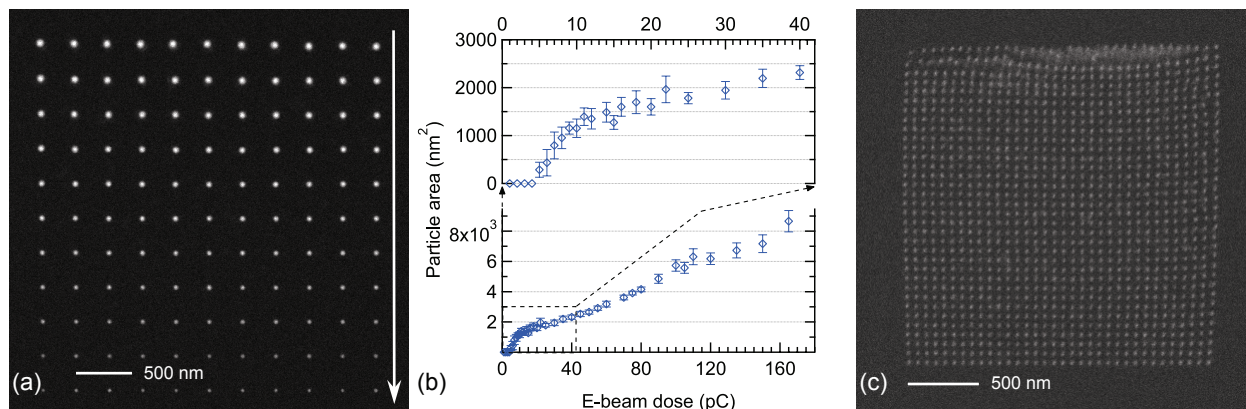


Fig. 2. (a) SEM image of representative array (350nm pitch) of Pt NPs deposited at different e-beam doses: NPs along a horizontal row have nominally equal doses, decreasing by 10pC with each row from top (110pC) to bottom (10pC); downward arrow indicates deposition sequence: top row first, bottom row last. (b) Lateral area averaged over all same-dose Pt NPs and plotted as a function of dose for all (lower panel) or a subrange (upper panel) of the investigated doses. (c) SEM image of dense array of small Pt NPs: 60nm pitch, ~25nm diameter.

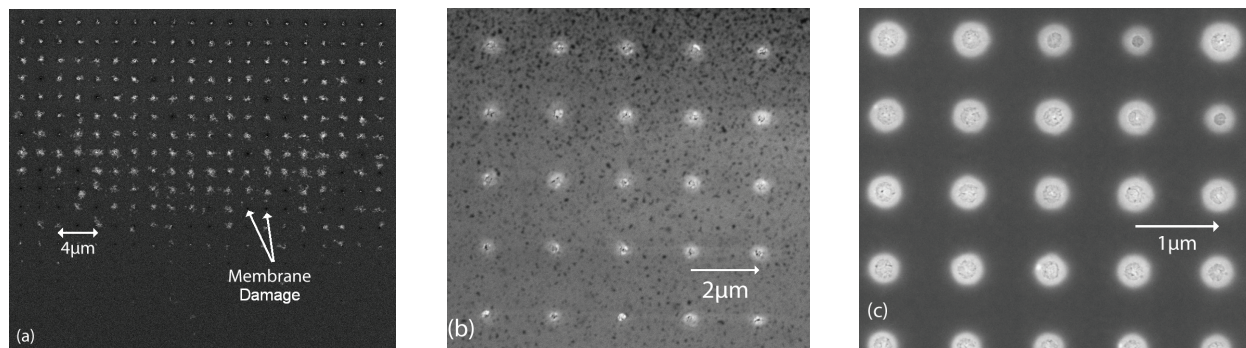


Fig. 3. (a) Au nanostructures deposited using single-pixel exposures with doses from 1-350pC (bottom to top) in 10 μM HAuCl_4 . Deposits have inconsistent structure, and membrane damage is evident in some areas. (b) Enlarged view of 250-350pC dose region of dot array with 25 pC/row using 1mM HAuCl_4 versus (c) same-dose region using 1mM NaAuCl_4 . Though still imperfect, more consistent structures were obtained from the neutral solution in (c).

Fig. 4. In contrast to the Pt deposition process, collateral deposition occurred for both (a) 1mM HAuCl_4 and (b) 1mM NaAuCl_4 . The neutral solution in (b) exhibited greater collateral deposition for the same pattern compared to the acidic solution in (a).

