Electron-Beam Induced Deposition of Transition Metals from Bulk Liquids: Ag, Cr, and Ni

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We are developing a new approach to electron-beam-induced deposition (EBID) that replaces gaseous precursors with bulk liquids. The liquids are separated from the vacuum environment of an electron-beam lithography system using an electron-transparent membrane. Liquid-phase EBID (LP-EBID) can provide enhanced purity compared to gas-phase processes, reduce substrate charging; and use more benign, stable, and cost-effective precursors. We have previously described the deposition of Au[1] and Pt[2-3] directly on polyimide membranes. Here we report our recent efforts to deposit other transition metals including Ag, Cr, and Ni. Deposition of these metals has introduced new challenges in terms of resolution and/or purity compared to previous studies.

Depositions were carried out from aqueous solutions on the polyimide membranes of a Quantomix WetSEM capsules. Silver nanostructures deposited from 1mM $AgNO_3$ are shown in Fig. 1a. Unintended collateral deposition between structures limited resolution to ~100-nm features on a 500-nm pitch. Energy dispersive x-ray spectroscopy (EDS) of larger structures (Fig. 1b) revealed that the composition was primarily silver with small sulfur contamination (~5 at.%) likely from the laboratory environment. A Cl peak also overlaps the Ag peak near 2640eV; thus, we cannot rule out chlorine contamination despite its absence in the precursor.

Cr was deposited from a 1mM solution of either $CrCl_3$ or $Cr_2(SO_4)_3$. Fig. 2a shows the highest Cr resolution obtained, a 125-nm half pitch dot array deposited from $CrCl_3$. Fig. 2b shows EDS analysis of deposits from both solutions indicating high contamination levels. Specifically $CrCl_3$ yields ~30 at.% Cr while $Cr_2(SO_4)_3$ yields ~50 at.% Cr. Contamination correlates with precursor composition, i.e. S and Cl are the primary contaminants for deposits from $Cr_2(SO_4)_3$ and $CrCl_3$ respectively.

As shown in Fig. 3a, Ni deposition from $NiSO_4$ yielded the highest LP-EBID resolution of any material thus far investigated with ~30nm features patterned on a 50nm pitch. The threshold dose for deposition of Ni on polyimide was similar to that required for Pt, ~3pC, for low density (1 μm pitch) dots. EDS analysis, Fig. 3b, showed a promising Ni:S ratio of approximately 6:1, but also contained Al and P peaks that cannot be attributed to the precursor.

The first e-beam induced deposition of non-noble metals, Ni and Cr, from aqueous solutions yielded excellent resolution. Contamination from precursor components is significant for Cr, but relatively small for Ni. The origin of several other contaminants remains to be determined. The deposition of Ag from aqueous solutions yielded good purity, but with collateral deposition similar to that observed for Au deposited from chloroaurate and sulfitoaurate complexes.[1]

1. G. Schardein, E. U. Donev and J. T. Hastings, Nanotechnology **22** (1), 015301 (2011).
2. E. U. Donev and J. T. Hastings, Nano Letters **9** (7), 2715-2718 (2009).
3. E. U. Donev and J. T. Hastings, Nanotechnology **20** (50), 505302 (2009).

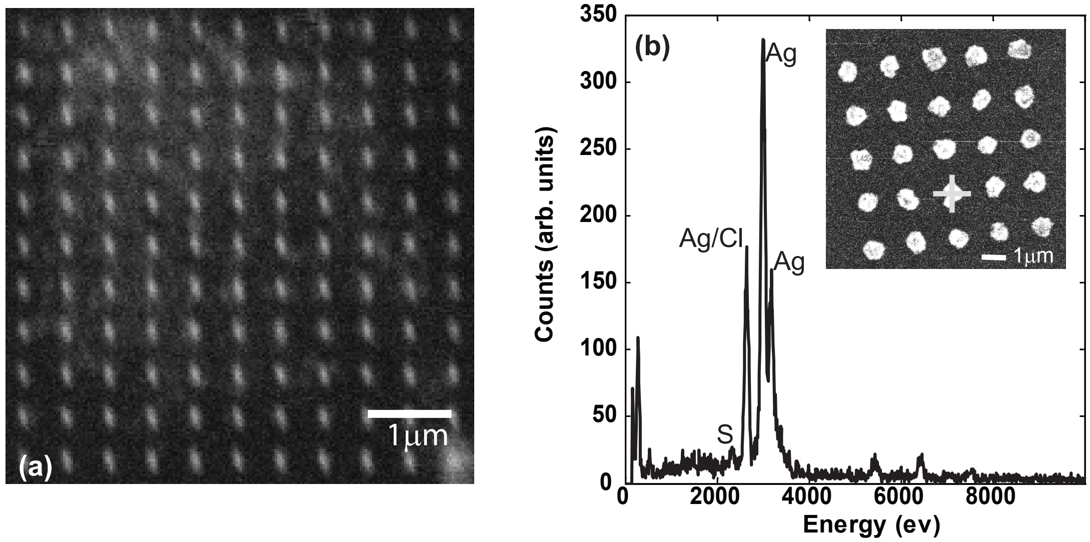

Figure 1. (a) 500-nm pitch Ag nanostructures deposted from 1mM $AgNO_3$ (aq). Note collateral deposition between features. (b) EDS spectra of larger Ag deposits (shown inset). Slight sulfur contamination is present and Cl cannot be ruled out.

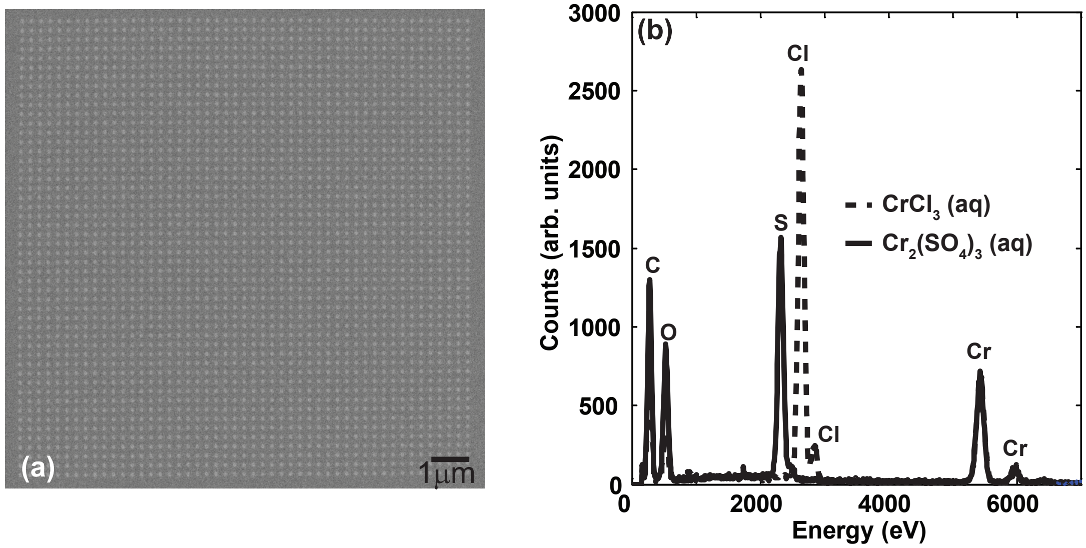

Figure 2. (a) 250-nm pitch Cr nstructures deposted from 1mM $CrCl_3$(aq). (b) EDS spectra indicate that contaminants correlate with precursor anions.

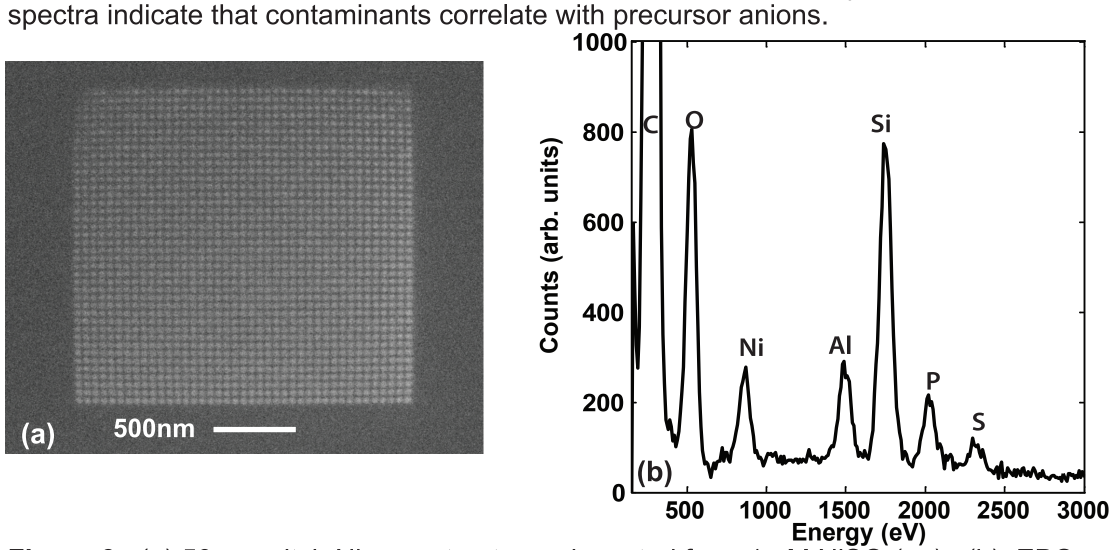

Figure 3. (a) 50-nm pitch Ni nanostructures deposted from 1mM $NiSO_4$(aq). (b) EDS spectra of larger Ni deposits. Ni:S ratio is ~6:1, but Al and P peaks remain unexplained.