Electron-Beam Induced Deposition of Highly Conductive Copper Nanowires from Bulk Liquids

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Electron-beam induced deposition is a position-controlled technique that can directly fabricate nanometer-sized structures in functional materials. In the standard process, a gaseous precursor delivers the desired substance to the substrate for deposition. However, the material purity from these precursors is typically poor[1] which often negatively affects the functional properties of the deposit. Recently, bulk *liquid* precursors have been investigated as promising reactants for high purity deposition without the need for post-processing.[2] In this work, we use aqueous solutions containing copper sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4) to deposit copper nanowires on oxidized silicon substrates in an environmental scanning electron microscope (ESEM). The ESEM permits deposition on bulk substrates without the need for a liquid cell.[2] Triton X-100 (a nonionic surfactant) or polyethylene glycol (1000 g/mol) were added to the solution to improve wetting and provide finer grained deposits.

Figures 1 and 2 show examples of patterned copper wires, their approximate dimensions, and their current voltage relationships from four-point probe measurements. The patterning conditions were 5.7 torr chamber pressure (water vapor), 3° C sample temperature, 30 kV accelerating voltage, 550 pA beam current, 20 μC/cm linear dose for wire in figure 1, and 25 μC/cm linear dose for wire in figure 2. No post-processing steps, such as thermal or e-beam annealing, were performed. The pattern fidelity of the lines is limited by collateral deposition of copper and precipitation of the additives near the patterns. However, the extracted resistivities are 8 μΩ•m and 50 μΩ•m. These are 5-6 orders of magnitude lower than that of as-deposited copper from gas phase reactants, 2-3 orders of magnitude lower than that of annealed materials,[3, 4] and within 2-3 orders of magnitude of bulk copper. We note one early study reported a resistivity of 0.036 $\mu\Omega \bullet m$ using the gaseous precursor (hfa)Cu-VTMS,[5] but this has not been borne out in later work. The low resistivity of deposits from $CuSO_4$-H_2SO_4 solutions without post-processing highlights the importance of overcoming the challenges associated with deposition via liquid precursors; such as collateral deposition, local delivery of the reactant, and control of liquid thickness.

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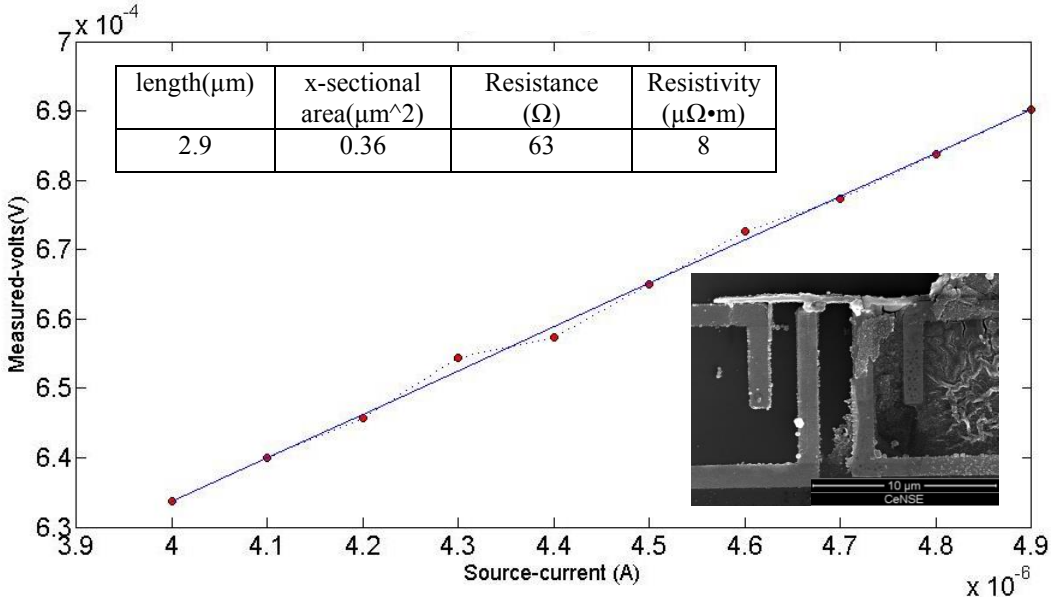
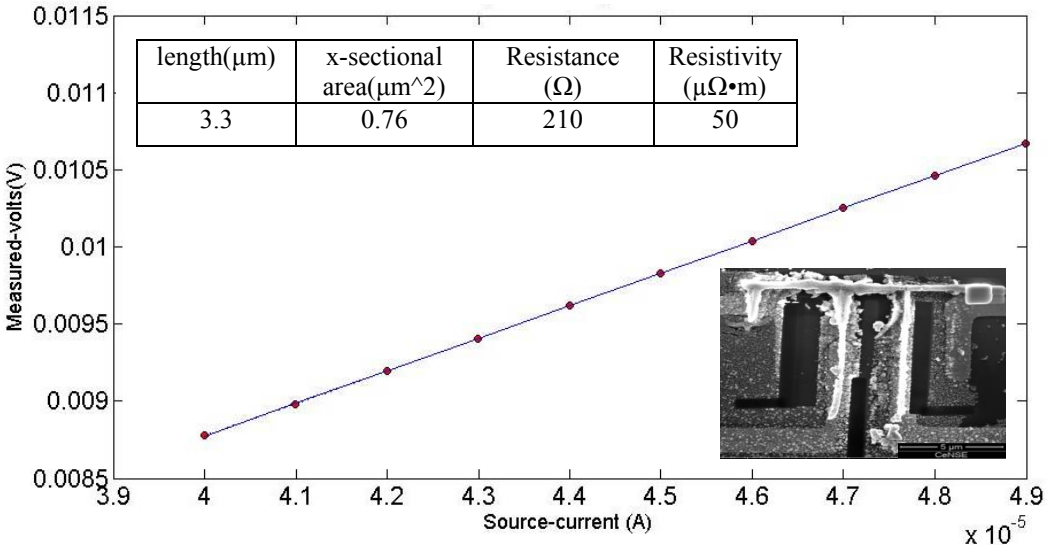
[1] A. Botman, J. J. L. Mulders, and C. W. Hagen, *Nanotechnology* **20** (2009).
[2] M. Bresin, A. Botman, S. J. Randolph, M. Straw, and J. T. Hastings, *Microsc. Microanal.* **20**, 376 (2014).
[3] A. Szkudlarek, A. R. Vaz, Y. C. Zhang, A. Rudkowski, C. Kapusta, R. Erni, S. Moshkalev, and I. Utke, *Beilstein Journal of Nanotechnology* **6**, 1935 (2015).
[4] A. Szkudlarek, A. Rodrigues Vaz, Y. Zhang, A. Rudkowski, C. Kapusta, R. Erni, S. Moshkalev, and I. Utke, *Beilstein Journal of Nanotechnology* **6**, 1508 (2015).
[5] Y. Ochiai, J. i. Fujita, and S. Matsui, *Journal of Vacuum Science & Technology B* **14**, 3887 (1996).



length(µm)	x-sectional area(µm^2)	Resistance (Ω)	Resistivity (µΩ•m)
2.9	0.36	63	8

Figure 1: I-V plot for a copper nanowire deposited from aqueous solution containing $CuSO_4$+H_2SO_4+Triton X-100. Inset left: Dimensions of nanowire and extracted resistivity averaged from three measurements of each. Inset right: Micrograph of nanowire and 4-pt probe structure. Solution residue and unwanted collateral deposition are visible around the right end of the wire.



length(µm)	x-sectional area(µm^2)	Resistance (Ω)	Resistivity (µΩ•m)
3.3	0.76	210	50

Figure 2: I-V curve for a copper nanowire deposited from aqueous solution containing $CuSO_4$+H_2SO_4+PEG 1000. Inset left: Dimensions of nanowire and extracted resistivity averaged from three measurements of each. Inset right: Micrograph of nanowire and four-point probe structure. Solution residue and unwanted collateral deposition are visible around the wire. FIB was used to ensure there were no alternative current paths, as well as to deposit platinum on the right end of the copper wire to ensure good electrical contact.