Supporting Information For

Reactive Silver Inks for Patterning High-Conductivity Features at Mild Temperatures

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1. Materials

Silver acetate (CH_3COOAg, *ReagentPlus*®, 99%) and formic acid (HCOOH, ACS Reagent, ≥88%) were purchased from Sigma-Aldrich (Milwaukee, WI). Ammonium hydroxide (Certified A.C.S. *Plus*, 29.3% assay) was purchased from Fisher Scientific (Pittsburgh, PA). All chemicals were used without further purification.

2. Ink Preparation and Chemistry

Reactive silver inks are synthesized by vortex mixing 1 g of silver acetate into 2.5 mL aqueous ammonium hydroxide at room temperature for 15 sec. Formic acid (0.2mL) is then titrated into the solution dropwise for 60 sec – vortex mixing after each drop. The solution changes in color from light orange to brown to grayish black indicating the rapid reduction of silver ions to large silver particles. The solution remains undisturbed for 12 h to allow the large particles to settle out yielding a clear supernatant that is decanted and filtered through a 200 nm syringe filter (Whatman Filters, Anotop 25). This clear solution, which contains 22wt% silver, serves as the reactive silver ink. The sediment is composed of large silver flakes (> 10 microns in size) corresponding to approximately 31% of the initial silver content used.

In a typical Tollens' reaction preparation, dilute silver nitrate and dilute sodium hydroxide precipitate a silver oxide intermediate that dissolves in an aqueous ammonia solution to create the Tollens' reagent. The typical reactions proceed as follows:

$$2AgNO_3 + 2NaOH \xrightarrow{H_2O} Ag_2O + 2NaNO_3 + H_2O$$

$$Ag_2O + 4NH_3 + 2NaNO_3 + H_2O \xrightarrow{NH_3/H_2O} 2Ag(NH_3)_2NO_3 + 2NaOH$$

Our modified Tollens' process is based on the following reactions:

$$2AgCH_3CO_2 + 2NH_4OH \xrightarrow{H_2O} Ag_2O + 2NH_4CH_3CO_2 + H_2O$$

$$Ag_2O + 4NH_3 + 2NH_4CH_3CO_2 + H_2O \xrightarrow{NH_3/H_2O} 2Ag(NH_3)_2CH_3CO_2 + 2NH_4OH$$

It is well known that Tollens' reagents require excess ammonia (≥ 4:1 ratio). The initial translucent red color that forms corresponds to silver oxide that has not been fully converted to

the Tollens' reagent. Upon addition of formic acid, unprotected silver is reduced to form particles (31% by weight) that must be removed by sedimentation. Approximately 40% by weight of the added formic acid is used in this process. The remaining formic acid neutralizes ammonium hydroxide by protonating the hydroxide to water and creating ammonium formate. The corresponding decrease in pH (from 14 to 10.6) enables more free ammonia to exist in solution, thereby creating the desired Tollens' reagent. Notably, our Tollens' reagent contains a high percentage of silver in solution compared to previously reported Tollens' reagent chemistries.

The reactive silver ink is composed of this final solution, which contains diamminesilver (I) cations, acetate anions and formate anions. As ink dries, the labile ammonia ligands evaporate allowing the silver cations to be reduced by the formate anions as well as acetic acid produced in solution from the uncomplexed silver that was previously reduced. The combination of formate and acetate ions with acetic acid results in a solution that reduces to silver and silver acetate particles upon drying at room temperature. The decomposition equations are provided below.

$$2Ag(NH_3)_2CH_3CO_2 + NH_4CO_2 \xrightarrow{\Delta} 2Ag + 5NH_3 + 2CH_3CO_2H + CO_2 + H_2O$$

$$2Ag(NH_3)_2CH_3CO_2 + NH_4CO_2 \longrightarrow Ag + AgCH_3CO_2 + 5NH_3 + CH_3CO_2H + CO_2 + H_2O$$

Upon annealing at 90°C, elemental silver is the only phase that remains due to the rapid evaporation of ammonia ligands and low boiling point reactants. In a sealed glass vial, the ink is stable at room temperature for 4-6 months. However, its stability can be extended beyond 6 months, if the ink is stored in an opaque vial and refrigerated.

3. Ink Printing

Direct ink writing is carried out using a 3-axis micropositioning stage (ABL 900010, Aerotech, Inc., Pittsburgh, PA), whose motion is controlled by computer-aided design software (A3200, Aerotech, Inc., Pittsburgh, PA.) The reactive silver ink is housed in a syringe (3 mL barrel, EFD, Inc., East Providence, RI) attached by luer-lok to a borosilicate nozzle (100nm tip diameter, World Precision Instruments, Inc., Sarasota, FL) that has been coating in a fluoropolymer (PFC504A-FS, Cytonix, LLC, Beltville, MD) to prevent wicking of the silver ink on the outside of the nozzle. An air-powered fluid dispenser (Ultimus V, EFD, Inc.) is used to pressurize the barrel and control the ink flow rate. Typically, a pressure of 50 psi is cycled on and off to fill the ultrafine nozzle with ink. The nozzle is then brought into contact with the substrate. The pressure is removed and patterning is achieved simply by moving the nozzle across the substrate surface at speeds ranging from 1-5 mm/s at 22-25°C. The printed features have varying widths depending on the degree of contact between the nozzle and the substrate. At this size (100nm diameter tip), the glass nozzles are highly flexible and can be brought into contact with the substrate and bent to nearly 90° without breaking (Figure S1). The printed electrodes are roughly 5-10 μm in width and 0.6 μm in height. A movie of the printing process is provided.

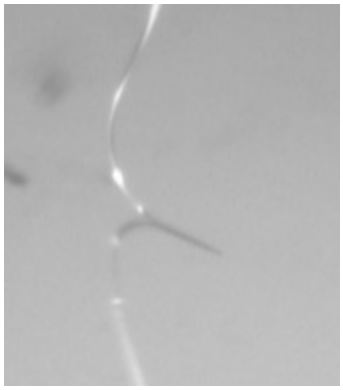

Figure S1. Optical image of glass nozzle (100nm in diameter) bending nearly 90° as it is driven into contact with the silicon substrate.

Inkjet printing is performed using a Fuji Dimatix DMP 2800 printer with 1 pL cartridges. The reactive silver ink is modified by adding 10% by volume of 2,3 butanediol, which serves as both a humectant and viscosifying aid. Ink droplets are produced using an ejection frequency of 2kHz at 30°C and they are dispensed with a spacing of 15 μm. A custom ejection waveform is generated in order to suppress satellite droplet formation and ensure reliable printing of the ink. Figure S2 shows a test pattern composed of printed features with minimum widths of 80-100 μm deposited on a glass slide.

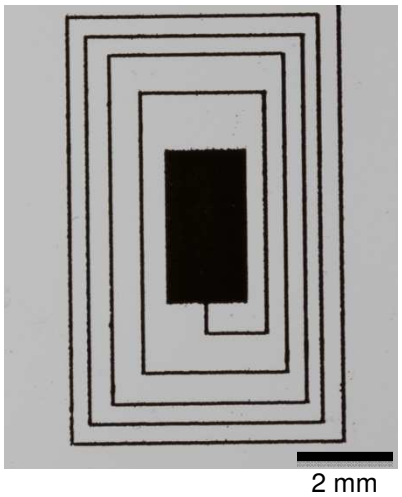

Figure S2. Optical image of a representative electrode pattern produced by inkjet printing the reactive silver ink onto a glass substrate.

As a final example, the modified, reactive silver ink is deposited onto an ethylene vinyl acetate substrate (75 mm x 25 mm) using an Aztec A7778 double-action airbrush. The ink is gravity fed into the airbrush via a 10mL cup and then dispensed by applying a pressure of 25 psi using an Aztec AC200 air compressor fitted with a moisture trap. Figure S3 shows a representative pattern produced by spraying the ink through a laser-cut stencil.

Figure S3. Optical image of silver electrode patterned produced by airbrush spraying the reactive silver ink onto an ethylene vinyl acetate substrate.

4. Characterization of Reactive Silver Inks

The UV/Vis absorption spectrum of the reactive silver ink is obtained using a CARY 500 Scan UV-vis-NIR spectrophotometer (Varian, Inc.) with a standard 1 cm liquid cuvette, with a background calibration run using deionized water.

Reactive silver ink viscosity is acquired using a stress-controlled rheometer (AR-G2, TA Instruments, New Castle, DE). Measurements are performed with a small double gap geometry that requires 5 mL of solution. All measurements are performed at 23°C using a solvent trap to prevent evaporation. The ink viscosity (η) is acquired as a function of shear rate (10-1000 s^{-1}) in a logarithmically ascending series.

Thermogravimetric analysis is performed using a Q50 (TA Instruments, New Castle, DE). An air environment is simulated by co-flowing 79% nitrogen and 21% oxygen at a volume rate of 100 mL min^{-1}. One sample is held at 23°C for 48 h, and the other sample was ramped at 10°C min^{-1} to 90°C and held at this temperature for 30 min. Each sample consists of 40 μL ink placed in a 90 μL alumina cup.

X-ray diffraction (XRD) is performed using a Siemens Bruker D5000 (Bruker, Inc., Madison, WI) with Cu K_α radiation and 2θ values from 10-140°. Low background holders are custom machined from an acrylic rod. Samples are prepared by allowing 2mL of reactive silver ink to either evaporate at 23°C for 24 h or anneal at 90°C for 15 min.

5. Characterization of Printed Silver Electrodes

Scanning electron microscopy (SEM) is used to image the surface of silver electrodes printed on silicon wafers using direct ink writing. The SEM images are acquired using a field emission microscope (Hitachi S4800). Figure S4 reveals significant variations in the printed line widths (~ 5-10 microns), which arise largely from the poor control over ink wetting and spreading. The higher magnification SEM images (insets) show the presence of fine particles that form during evaporation and subsequent annealing of the printed electrodes.

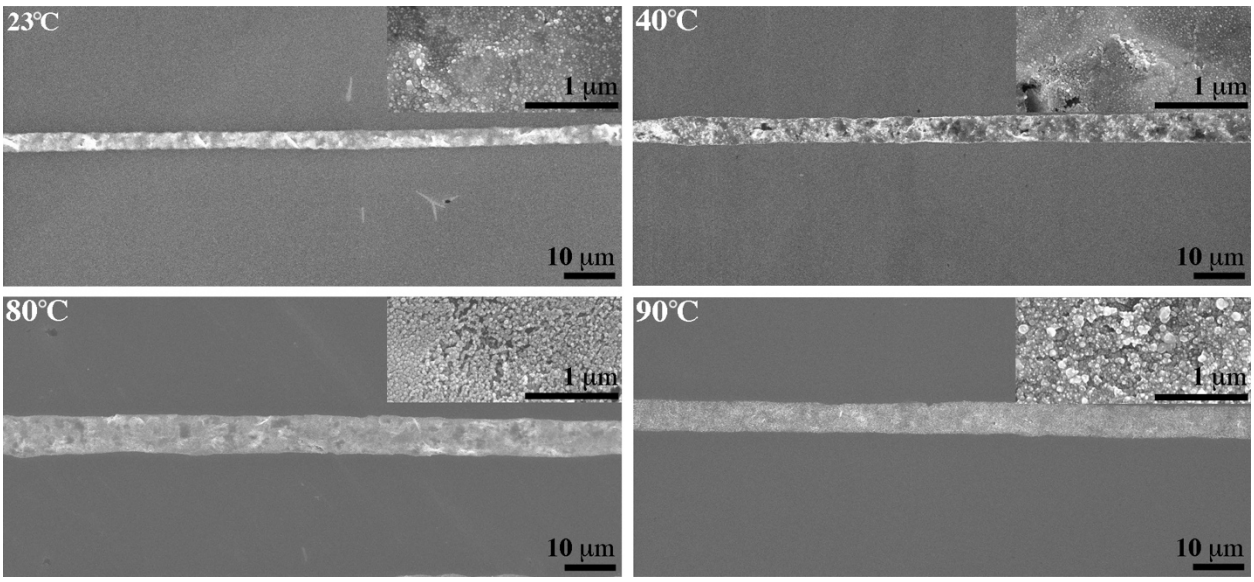

Figure S4. SEM images of patterned silver electrodes produced by direct ink writing through a 100 nm nozzle [Insets: SEM images of each electrode surface at higher magnification].

The surface roughness of the printed silver electrodes produced from direct writing of the reactive silver ink is measured using atomic force microscopy (AFM). These measurements are performed using an Asylum Research MFP-3D in tapping mode at 0.5 Hz at a 256-line resolution with Tap300Al-G silicon tips purchased from Budget Sensors. The root-mean-square roughness of the printed electrodes dried at 23°C is 92 ± 12 nm. This value decreases upon annealing to 84 ± 8 nm, 61 ± 7 nm, and 50± 5 nm at 40°C, 80°C and 90°C for 15 min, respectively.

The electrical resistance of the printed electrodes produced by direct writing of the reactive silver is measured using a two-point probe method (Keithley 2400 with a voltage/current sweep). For comparison, the electrical resistance of drop-cast films is also measured using a RM3-AR four-point probe coupled to a multiheight probe with a cylindrical probe head (Jandel Engineering Ltd., Linslade, UK). The films are prepared by casting 0.4 mL drops of the reactive silver ink onto glass slides. The printed electrode height is measured by AFM, while the film height is measured using a Dektak 3030 (Veeco, Inc.) contact profilometer. Their electrical conductivity is determined by taking the inverse of the sheet resistance in $\Omega\square^{-1}$ multiplied by height (cm). Note, the contact resistance between the tungsten probes (Signatone) is measured and subtracted from these data. The electrical conductivity of the printed silver electrodes and films dried at 23°C and annealed at varying temperatures is shown in Figure S5. An annealing temperature of 90°C is required to achieve an electrical conductivity equivalent to that of bulk silver.

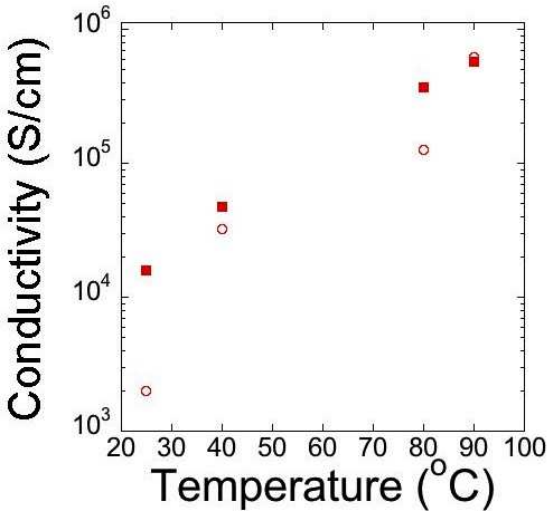

Figure S5. Electrical conductivity of printed electrodes (closed squares) and drop-cast films (open circles) as a function of temperature.

Finally, we assessed how well the reactive silver inks adhered to several substrates, including glass, cellulose acetate, cellophane, polyimide, and PET films that are pre-cleaned with isopropanol, acetone, or deionized water. Scotch tape is used to test adhesion by applying half of the tape to the bare substrate and half to regions patterned with the ink. After removing the tape, the samples are inspected to visually to determine the amount of silver removed from the substrate. All plastic films were also flexed and bent with no observed decrease in adhesion of the silver features.

Complete Ref. 15:

(15) Kim, D.; Viventi, J.; Amsden, J.; Xiao, J.; Vigeland, L.; Kim, Y.; Blanco, J.; Panilaitis, B.; Frechette, E.; Contreras, D.; Kaplan, D.; Omenetto, F.; Huang, Y.; Hwang, K.; Zakin, M.; Litt, B.; and Rogers. J. *Nature Mat.* **2010**, 9, 511-517.