

Supplementary Information for

High-Speed, Solution-Coatable Memory Based on Cu-SiO₂ Core-shell Nanowires

Patrick F. Flowers, Matthew J. Catenacci, Benjamin J. Wiley

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1. Supplementary Methods
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Supplementary Methods

Chemicals Used. Sodium hydroxide was purchased from NOAH Technologies Corporation. Hydrazine (N_2H_4) 35 wt% in water was purchased from GFS Chemicals. Copper(II) nitrate hemi(pentahydrate) was purchased from Alfa Aesar. Ethylenediamine (EDA), N, N-diethylhydroxylamine (DEHA), and polyvinylpyrrolidone (PVP, MW = 10,000), were purchased from Sigma-Aldrich. Glass microscope slides (7.5 cm \times 2.5 cm \times 0.1 cm) were purchased from McMaster-Carr. Nitrocellulose was purchased from Scientific Polymer. Acetone, 190 proof ethanol, and glass microscope slides (7.5 cm \times 2.5 cm \times 0.1 cm) were purchased from VWR. All chemicals were used as received.

Synthesis of Cu NWs. Flasks and stir bars were cleaned with concentrated nitric acid, thoroughly rinsed with deionized water, and dried in an oven at 80 °C before use. Once dry, the flasks were allowed to cool to room temperature before any reactants were added.

Cu NWs were synthesized by implementing a 50x larger scale version of the reaction described previously by Wiley et al.^[1] NaOH (1 L, 15 M), $\text{Cu}(\text{NO}_3)_2$ (50 mL, 0.1 M), and EDA (7.5 mL) were added to a round bottom flask. This mixture was heated at 50 °C and stirred for 15 minutes. The solution was then swirled vigorously by hand to ensure adequate mixing of the EDA. Hydrazine was then added (1.25 mL, 35 wt%) and the mixture was stirred for 5 minutes. After 5 minutes, stirring was discontinued and the reaction was allowed to continue for 1 hour. After the reaction was complete, the contents of the round bottom flask was transferred to a separatory funnel where a 3 wt% PVP and 1 wt% DEHA solution in DI H_2O was used to wash the nanowires. Upon addition of PVP/DEHA solution, a large nanowire aggregate was formed. This aggregate was soaked in PVP/DEHA solution and carefully rinsed. The aggregate was then shaken to disperse the nanowires and stored under Argon in a solution of DEHA (1 wt%) and PVP (3 wt%) at room temperature to prevent oxidation.

Cu NWs were coated with amorphous silica shells according to an adapted version of the reaction described by Koboyashi et al.^[2] In our adaptation, 7.7 mg of Cu nanowires were rinsed 1x with a solution of 3 wt% PVP in DI H_2O , and transferred to a 20 mL scintillation vial containing 10.5 mL EtOH and 1.7 mL DI H_2O . While stirring, 282 μL of dimethylamine (40 wt%, Sigma-Aldrich) and 40 μL of TEOS

(tetraethylorthosilicate, 98%, Acros Organics) were added to the Cu nanowire suspension, and the reaction mixture was stirred for 10 minutes during the growth of the SiO₂ shells. The nanowires were then rinsed 1x with a 50/50 EtOH/DI H₂O solution and characterized by TEM (FEI Tecnai G² Twin) and SEM (FEI XL30 SEM-FEG).

Ink formulation. A nitrocellulose-based ink was used to print the nanowires into a well-dispersed thin film. To prepare the ink, a 3 wt% solution of nitrocellulose in acetone was mixed with a 0.5 wt% solution of Zn(OAc)₂ in EtOH in a 1:1 ratio. The Zn(OAc)₂ acts as a binder between the nitrocellulose and silica. After the SiO₂ coating, core-shell nanowires were rinsed with 190 proof EtOH 1x, followed by our ink formulation 1x, and then finally suspended in ink at the desired concentration for printing.

Electrode fabrication and printing of the memory. Electrodes for probing the memory were fabricated on glass microscope slides. Patterning of electrodes was accomplished using traditional photolithographic processes. Gold electrodes were deposited by electron beam evaporation and copper electrodes were deposited via sputtering. The core-shell nanowires were dispersed in our ink formulation and printed from solution directly onto the electrodes. After drying, the nitrocellulose was removed from the film by heating under forming gas (4.926% Hydrogen, 95.074% Nitrogen) at 200 °C in a tube furnace for 30 minutes. After cooling, the nanowire/ink formulation was printed directly onto the substrate from solution using a knife blade.

Electrical Characterization of Nanowires. All resistance measurements as well as the voltage sweeps in Fig. 2 were performed with a Keithley 2400 SourceMeter®. Pulses for characterization of the switching speed were generated with a Hewlett Packard 8112A 50MHz pulse generator, and a Hantek DSO – 5200A oscilloscope was used to record the results. Characterization of the switching speed was performed with the circuit shown in Fig. S4a. The voltage applied by the pulse generator was detected by channel 2 of the oscilloscope while channel 1 was used to measure the change in voltage through the 200 KΩ resistor in series with the memory. When the memory is in the OFF state, channel 1 of the oscilloscope will read a 0 V drop across the 200 KΩ resistor. During the write process, the resistance of the memory cell decreases by several orders of magnitude, causing the current through the memory to increase. The 200 KΩ resistor ensures the current flowing through the memory does not continue to climb to damaging levels. As the

memory is switched on, the voltage across the 200 K Ω resistor increases while the voltage across the memory is simultaneously limited to 50-75 mV as determined by the value of the applied write pulse (10 or 15 V). In this way both the current and the voltage are limited in the memory, thus completing the transition. The current flowing through the memory was calculated by dividing the voltage detected by the oscilloscope by 200,000 Ω . This current response through the memory is observed from channel 1 on the oscilloscope while monitoring the input voltage on channel 2. A higher input pulse (as compared to the voltage sweep cycle testing) was used to overcome the effects of parasitic elements in the switching speed test circuit. A calibration curve was created to correct for the variation of the ON state resistance of the memory (Fig. S4b). To generate this curve, the resistance of one channel was varied with a variable resistor and the difference between the total resistance of channel 1 and channel 2 was recorded (x-axis). The time delay between the current and voltage pluses was then measured for each of the resistance differences between channels 1 and 2, and plotted on the y-axis. When the memory cell was switched on, the difference in resistance between channel 1 and channel 2 was measured for each individual test and a correction factor was applied based on the calibration curve to shift the current response curve. An example correction is shown in Fig. S4c. After the correction was applied, the time delay between when the applied voltage and current response reached 90% of their maximum value was recorded as the write speed for the memory. A total of 4 samples were tested and all of their measured write speeds were comparable as shown in Fig. S5.

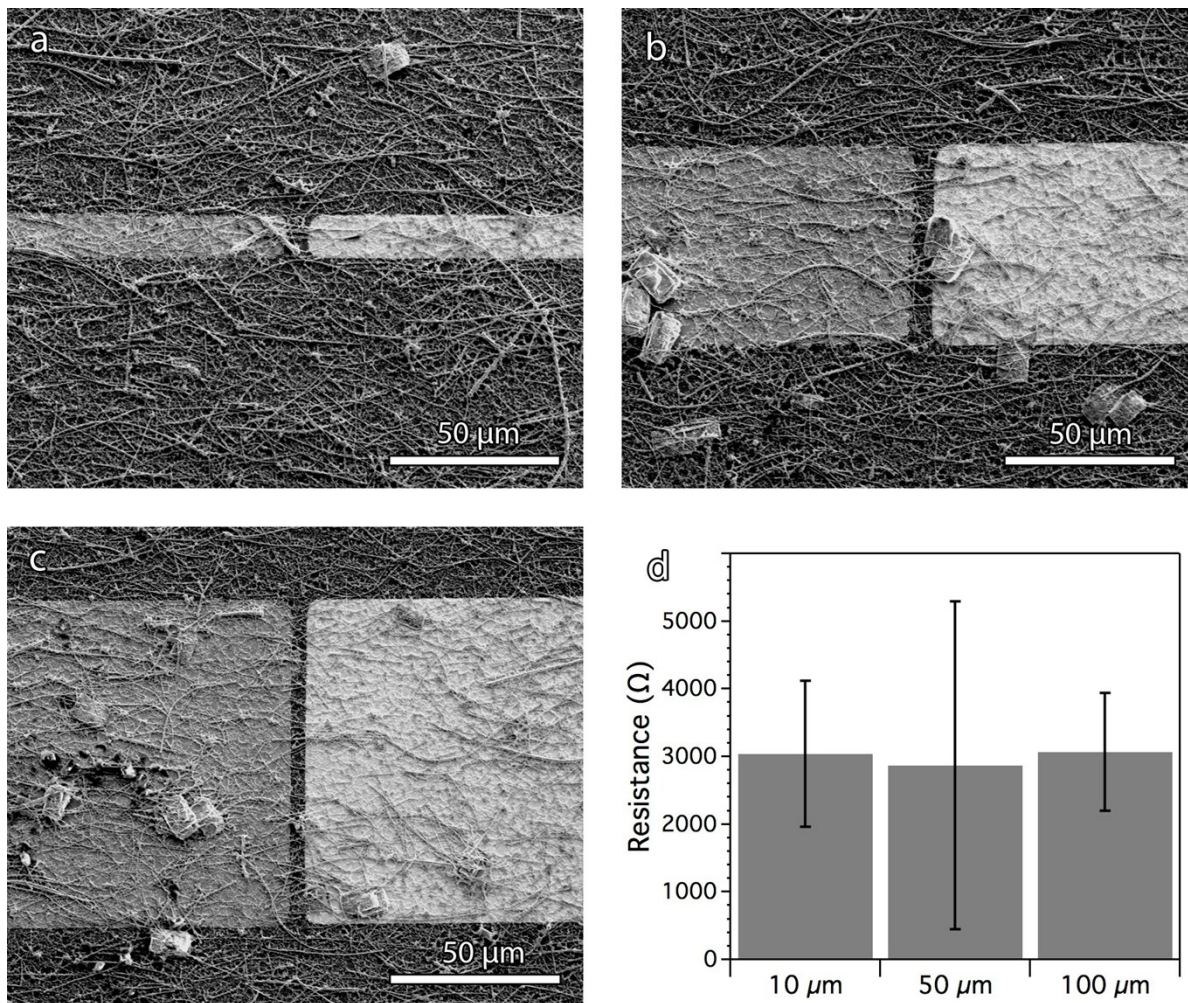


Figure S1. a) 10 μm, b) 50 μm, c) and 100 μm electrodes were used to conduct 100 write/erase cycles. d) The size of the electrodes has no significant effect on the ON resistance. Scale bars indicate the standard deviation of 100 measurements.

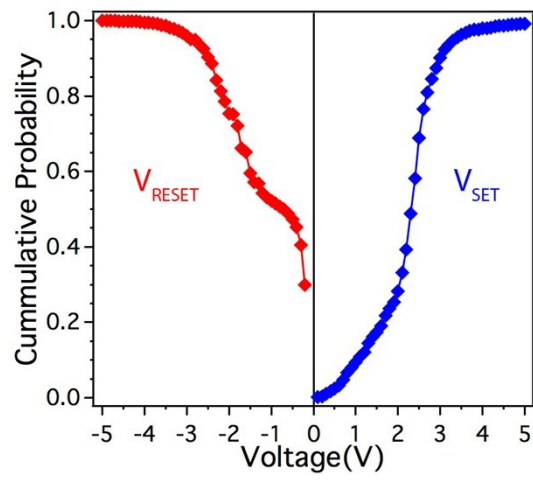


Figure S2. Cumulative probability distribution of V_{SET} and V_{RESET} over 10,000 cycles.

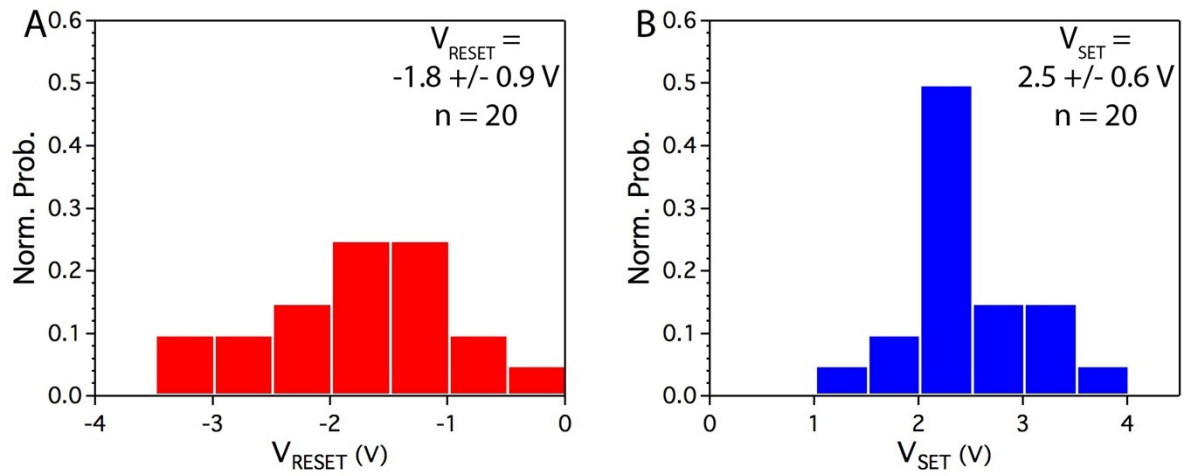


Figure S3. Twenty samples were tested to determine how the threshold voltages varied from sample to sample. The average of 100 switching cycles for each sample was recorded and populated into the histogram to show the distribution of a) V_{RESET} , and b) V_{SET} amongst different samples.

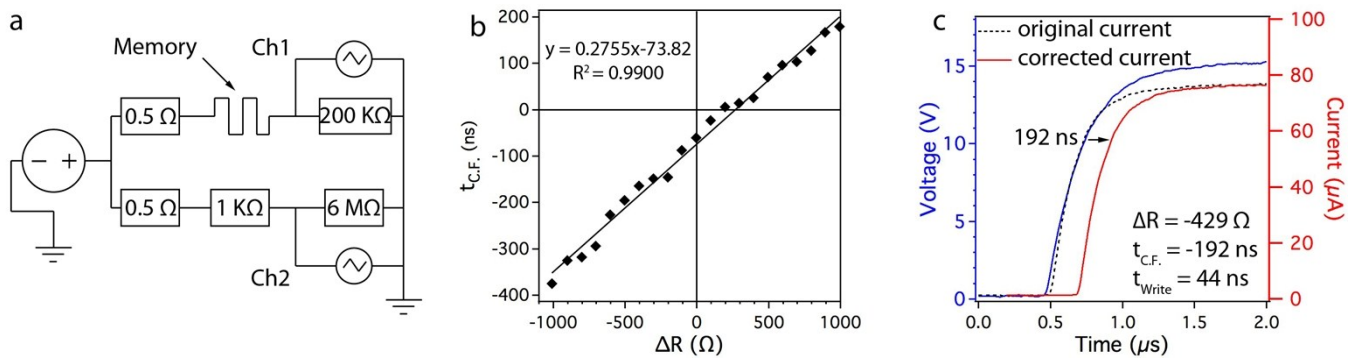


Figure S4. a) Test circuit wherein channel 2 of an oscilloscope records a voltage pulse applied to the circuit while channel 1 of the oscilloscope is used to observe the change in voltage across a 200 K Ω resistor. This change in voltage is directly related to the current response as the memory switches ON which is easily calculated by dividing the measured channel 1 voltage by 200,000 Ω . b) The calibration curve relates the difference in resistance between the memory and 1 K Ω (x-axis) to the time delay between the voltage and current pulses. c) An example is shown wherein a 15 V pulse applied to the test circuit as measured with channel 2 of the oscilloscope is shown in blue. The calibration curve was used to shift the original current response curve (dotted line) forward by 192 ns (red line) to account for a measured 429 Ω difference between the 1 K Ω resistor and the memory after it had been switched ON.

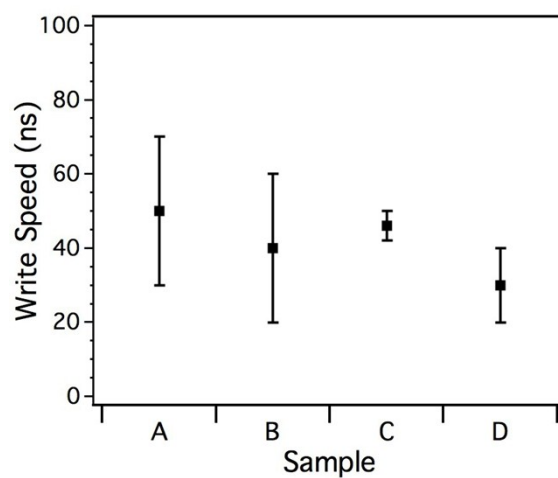


Figure S5. Switching speed test results for 4 different samples. Sample A corresponds to Figure 4 wherein a ~ 15 V write bias was used ($n=15$). A 10 V bias was used on Samples B – D ($n=3$).

REFERENCES

- [1] S. Ye, A. R. Rathmell, Y.-C. Ha, A. R. Wilson, B. J. Wiley, *Small* **2014**, *10*, 1771.
- [2] Y. Kobayashi, H. Katakami, E. Mine, D. Nagao, M. Konno, L. M. Liz-Marzán, *Journal of Colloid and Interface Science* **2005**, *283*, 392.