CuS and AgS Solid-Electrochemical Cells as Non-Volatile Memory Devices

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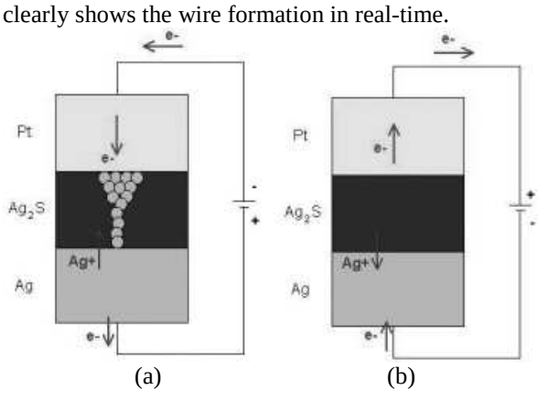
Metallic nano-wires, either formed in break-junctions or between a scanning tunneling microscope tip and suitable substrates, have been studied and used in molecular electronics and quantized conductance measurements. We show for the first time that silver nanowires can be reversibly grown between silver (or copper) and gold electrodes through a silver sulfide (or copper sulfide) layer with wires exhibiting fractal geometry and spanning inter-electrode distances of up to 1 cm through the solid-electrolyte (silver sulfide or copper sulfide) layer (figure 1). The application of a sufficiently large negative voltage to the gold electrode injects free electrons into the silver sulfide film initiating an electrochemical reaction $Ag^+ + e^- \rightarrow Ag$ forming elemental metallic silver at the interface between the gold electrode and the silver sulfide film. The silver continues to accumulate forming a metallic bridge between the two electrodes (figure 1c). This effect is reversed by applying a voltage of opposite polarity to the gold electrode, breaking the metallic bridge. Similar process occurs in copper sulfide films. A video clip clearly shows the wire formation in real-time.



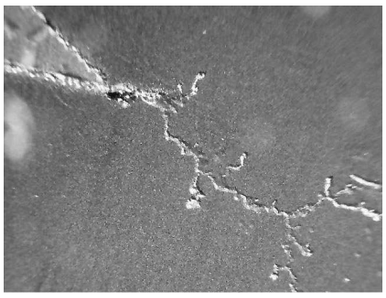

(c)

Figure 1 Schematics of a) Silver nanowire formation and b) dissolution process. c) SEM of silver wire growth through a 5mm silver sulfide gap. The gold electrode is shown in top left while the silver electrode is not shown but it is located in bottom right.

Current versus voltage characteristics obtained using conducting atomic force microscopy is shown in figure 2. At 0.6 volts, the film becomes conducting and stays conducting when the scan polarity is reversed. When the tip substrate voltage reaches –0.7 V, the film turns off and stays off for subsequently more negative voltages. The Switching behavior shown in figure 2, can be used in non-volatile memory devices. Owing to their very simple geometry, these devices based on solid-electrolytes are highly scaleable, and low power. To explore their memory applications, silver sulfide switches were fabricated in a grid formation consisting of parallel silver wires on which thin films of silver sulfide were deposited and crossed by gold or platinum grids. Such grids were interfaced with conventional CMOS circuitry that performed multiplexing and buffering functions and forming memory arrays. Typical switching times less than 1 ms were observed. Using current state-of-the-art photolithography techniques to fabricate such grids, memory arrays of silver sulfide switches (0.1 μm x 0.1 μm) could be fabricated with a device density on the order of 10^8 /cm^2. The theoretical limit of device density with devices on the order of a few hundred silver atoms in diameter is on the order of 10^{12}-10^{13}/cm^2. The switching time can be reduced to nanosecond range by using very thin solid electrolyte layers.

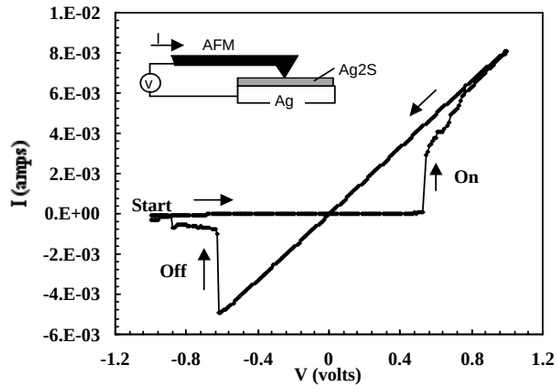


Figure 2 Current versus voltage characteristics of Ag_2S on Ag using a conducting AFM tip. The voltage polarity in this figure is given at the Ag substrate.

Moreover, quantized conductance levels, similar to those found in break-junctions, were also observed in silver sulfide devices as shown in figure 3. It is important to note that the system we present here has the advantage that the nanowire formation is electric field induced and the system is mechanically stable and reversible. These quantized conductance levels can be used in multi-level memory cells.

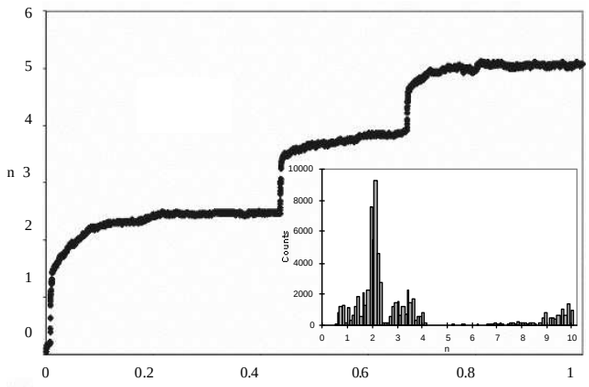


Figure 3 Conductance quantization index n (=I/VG_0, where G_0=2e^2/h) as a function of time at V=+0.1 V (the same polarity convention as in figure 2). As the wire form, the conductance increases in steps as a function of time. The inset shows the index histogram. Most events are bunched around 0.7 G_0, 2 G_0, and 10 G_0.