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Controlled directional growth of silver microwires on a solid electrolyte surface

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A silver microwire was formed on a silver sulfide surface in a directional and reversible manner. This wire formed upon applying an electric field between a tip-less atomic force microscopy probe placed on the Ag_2S surface and a grounded silver electrode embedded in the surface. The process was studied in real-time with optical microscope and a discussion was provided on how the morphological instability was violated. A numerical model based on the mixed ionic-electronic transport was developed to study the observation and a good match of growth rates was found. The fast metal wire growth phenomenon observed here has potential in applications for electronics as well as plasmonic sensors and waveguides © 2010 American Institute of Physics.

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The migration of ions in a solid electrolyte in electrochemical gradient is a well-understood fundamental behavior of charge carrier species in solid electrolytes. The observation of such coupled mass-charge transport along with the dissolution and deposition of anode and cathode, respectively, has led to explanations for the local electronic short-circuit and resistance degradation in batteries^{1,2} and understanding in the resistive switching behavior along the conducting paths in solid electrolytes.³⁻⁵ The growth of metal, as a result of such deposition, is most of the time dendritic, and an exact prediction of morphology is not possible. Such nature can be explained by a morphological stability analysis.⁶⁻⁹ Asperities on the cathode-solid electrolyte interface increase the local electric field and thus metal ion flux into them. The result is the growth front at the tips moves faster than the surrounding and the interface is morphologically unstable.

Here we report the observation of a reversible, directional growth of a silver microwire between two electrodes placed on a silver sulfide surface upon the application of a voltage between the two. Silver sulfide substrate was synthesized according to the method used in our previous work¹⁰ and then mechanically polished progressively to a mirror finish. An electrode configuration as shown in Fig. 1 was used wherein a tip-less conductive AFM cantilever (with a $5 \times 5 \times 0.2 \mu\text{m}^3$ Pt contact pad deposited on the cantilever by focused ion beam) was placed on the silver sulfide surface as an electrode while an embedded Ag inclusion was grounded. The experiment was carried out on a NanoScope multimode AFM and the electrical bias on the AFM cantilever were applied by the internal circuits of the AFM.

As a result of applying -50 mV of bias to the AFM probe, a wire was observed to grow from the probe toward the grounded electrode, as seen in the series of images from 12 to 13 s shown in Fig. 2(a). The speed at which the growth front moves was close to $100 \mu\text{m/s}$. When the bias was reversed, 50 mV at the AFM probe, the wire was seen retract from the metal inclusion and disappear in about 1 s [also shown in Fig. 2(a), from 19 to 20.2 s]. When the bias was

again reversed (50 mV at the AFM probe with respect to the grounded metal inclusion), the wire grew out again, but with a much faster rate. Within 200 ms, the wire was seen between the two electrodes in the same trace where the previous wire had been. The speed of this second-time growth was about five times faster. After the wire connected to the metal-inclusion electrode, the wire grew thicker until the bias was removed from the AFM probe. This phenomenon was repeated for several times.

We found that although the growth rates of so-grown wires increase with higher applied electric field, the lateral dimension of the silver wires remained around $5 \mu\text{m}$ when they were initially formed. We propose that this independence of wire width on applied electric field is due to the fact that the directional wire forming observed here is growth dominant because of the high electric field at the growth front. Therefore, the size of the growth front and the initial wire size are limited to the size of the Pt contact pad used as an electrode. As the wire forms, more ions are allowed to migrate toward the wire and deposit on it. As a result, the wire widens.

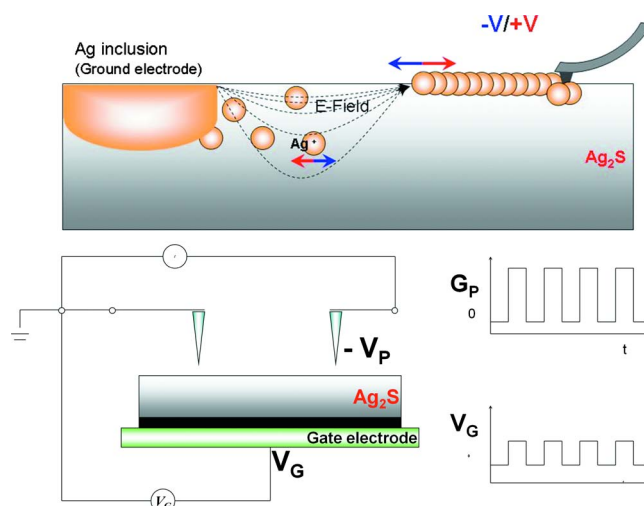


FIG. 1. (Color online) (a) Illustration of how a silver bridge can form on a silver sulfide surface between an ion source and an electrically biased electrode. (b) Experimental configuration for surface electrode bridging on silver sulfide.

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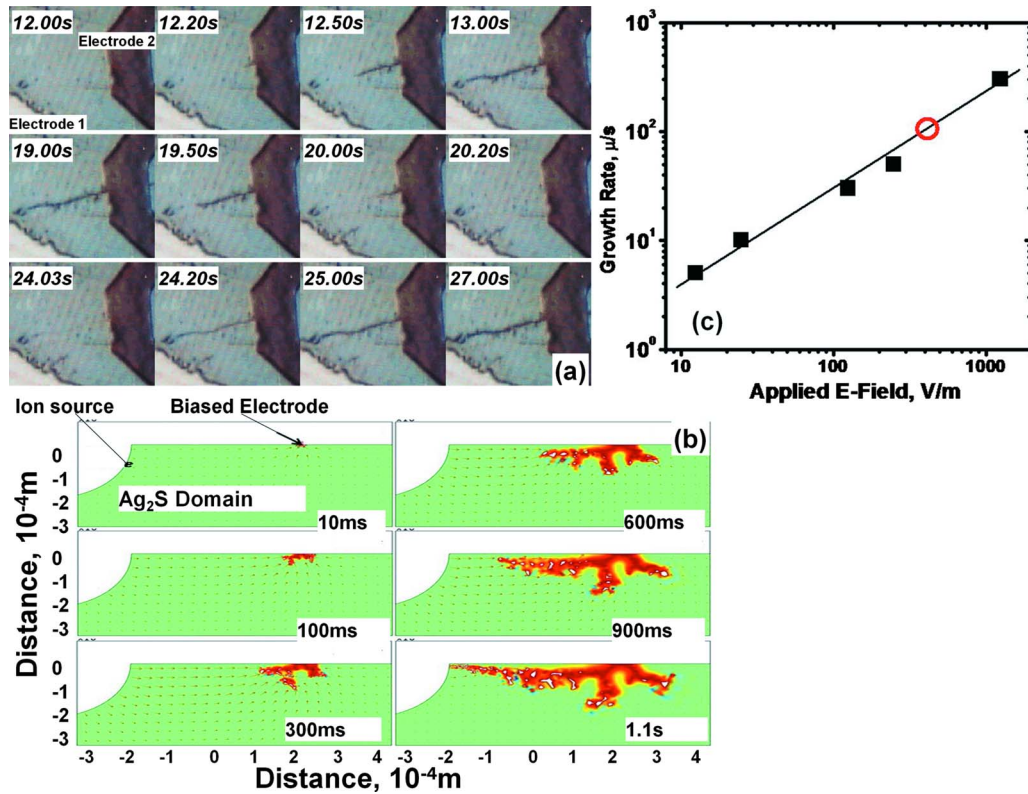


FIG. 2. (Color online) (a) Series of optical images of the reversible silver wire growth on silver sulfide surface. (b) Numerical Study of directional Ag wire growth. (c) Numerical estimation of Ag wire growth rate.

The results shown here have never been reported before since the morphology of the growth of an electrode is known to be unstable and cannot be predicted.^{6–8} The growth of silver whiskers from cathodes have been reported several times, but it has been either of dendritic nature, spreading out from the cathode with no preferential directions, or linear growth in free space under strong electric field.^{9–12} Here we propose that the directional growth of the silver whisker could be a result of the electric field pattern formed between the two electrodes, as well as the fact that a silver inclusion as the ion source was available in the solid electrolyte. As shown in Fig. 1(a), the linear path between the two electrodes has the highest field gradient and it could be the dominant path in which the dissolved silver ions migrate toward the AFM probe. As the growth front of silver wire moves in this linear path, the distance between the metal inclusion and the silver wire growth front reduces rapidly, increasing such effect even more. Along with this condition is the fact that supply of ions is mainly from the metal inclusion and is confined in a range of directions directly between the two electrodes. The end result is a directional growth of a silver wire.

The result here suggests that microscale Ag wires can be precisely grown/erased at desired location in a highly controllable manner for electronics applications. In addition, as compared to the rate of silver film observed in Peppler's work,¹³ the growth rate of silver wire front observed here is more than two orders of magnitude higher, even though the mobility of silver in silver sulfide is orders of magnitude smaller than that in single crystal silver bromide at 570 K,¹⁴ and that silver sulfide is a mixed-conductor with a transference number of close to 0.01 at room temperature, we propose that the fast speed of the silver wire growth front could

be a result of the enhanced ionic transport properties of silver in silver sulfide near the surface as suggested in Karashanova's work.¹⁵

To further study such growth mechanism, we developed a numerical model to account for the transport properties in mixed ionic-electronic conductors such as silver sulfide. As shown in Fig. 2(b) the simulation domain represents the cross-section along the probe-ion source plane. While a -50 mV electrical bias is applied to the electrode-electrolyte domain interface [as indicated in the snapshots in Fig. 2(b)], the semicircle is grounded. As captured by the numerical model, the growth starts with somehow dendritic nature due to the competition between nucleation and growth, but eventually becomes directional. As discussed earlier, the reason lies in the sharp increase in the electric field between the ion source and the growth front headed toward it as growth proceeds. Also evident is the suppression of other growth fronts due to such electric-field distribution change, confining the dendrites to the vicinity of the biased probe. Through this numerical model we also found good agreement between the experimentally observed growth rate and the numerical predictions: $100 \mu\text{m/s}$ at 500 V/m . Further, we also found this numerical model captures our experimental observation that the widths of the wires are more or less independent of applied electric field, but dependant on the size of the electrode, as well as the length of time in which the applied potential remains after the metal wires are formed.

To extend this observation to practical applications such as break-junction device construction, an electrode configuration as shown in Fig. 1(b) was used wherein two tungsten probes were placed on a silver sulfide surface and a third electrode was used as a gate to regulate the migration. A square-form gate voltage between 0 and 600 mV at 0.8 Hz

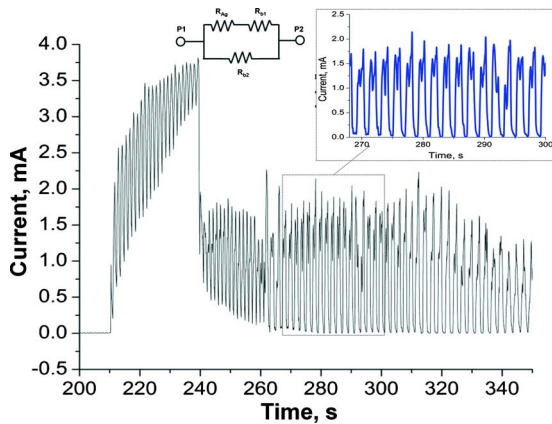


FIG. 3. (Color online) Switching behavior of silver wire grown between the two electrodes on a silver sulfide surface.

was applied and a constant potential of 10 mV was maintained between the two tungsten probes with a potentiostat (Gamry, model Reference 600) and the current monitored. A silver wire was observed to grow between the two probes, and current between them was also observed to change during the wire growth. As the wire reaches the anodic probe, the current was observed to increase by three orders of magnitude. As seen in Fig. 3, from 210 to 240 s the current in the probing circuit changed increased from around tens of microampere to around 4 mA, indicating three order of magnitude increase in conductance. The rate of growth here is around $20 \mu\text{m/s}$, roughly an order lower than the rate observed when both the cathode probe and the ion source are on the surface. Given that the electric field in the two cases are similar, this suggests the rate of silver wire growth, or silver transport rate, along the electrolyte surface is higher than that in the silver sulfide bulk.

To examine the resistive switch behavior, when the two probes were visually seen bridged, the gate voltage was then shifted to switching between -0.3 and $+0.3$ V with the same frequency. The current between the two W probes was observed to come to a steady switching behavior with a conductance change of three orders of magnitude, and the switching in phase with the gate voltage as shown in Fig. 3.

The increase in conductance between the two probes can be explained by considering an equivalent circuit between the two probes shown in the inset in Fig. 3. The resistance between the two probes can be approximated as two resistors, R_{Ag} and R_{b1} , in series and then in parallel with another resistor R_{b2} . R_{Ag} is the resistance of the silver wire formed, and R_{b1} is the bulk resistance of silver sulfide substrate between the growth front of the silver clusters and the probe with higher potential that the structure is growing toward. R_{b2} is the resistance of any other path in which electrons would travel if the resistance was lower than the linear path connecting the two probes. Electric current initially flows through the lower half of the equivalent circuit when there is no silver cluster growth, given the R_{Ag} value is infinity. As silver wire starts to form R_{Ag} drops to a low value corresponding to the resistivity of silver. In addition, R_{b1} value also decreases due to the reduction in the distance between the growth front and the target probe. The reduction in values of R_{Ag} and R_{b1} causes the decrease in the resistance of the upper half of the circuit. As a result of the resistance distri-

bution change, more current flows through the upper half. As the silver grows further, R_{Ag} remains more or less the same as the thickness of the wire increases but the length increases. R_{b1} , on the other hand, further decreases to zero as silver cluster growth reaches its target probe. At this point, almost all the current flows through the upper half of the equivalent circuit as the silver bridge's resistance is orders of magnitude lower than that of the bulk resistance of silver sulfide, R_{b2} .

The results here also suggest that the surface Ag wire growth seen here might have been a result of the effect of restricting the transport of Ag to near-two-dimensional (2D) region in the first case where the ground electrode and the ion source were both on the surface. As compared to the second case where in the gate potential was the main driving force for ion transport, the near-2D transport has lower energy and higher probability for transport in a preferential direction than that of the three-dimensional transport in the second configuration.

Directional and reversible micro-scale silver wire growth was observed on a silver sulfide surface between an ion source and an AFM probe. We proposed that it was due to the electric field pattern formed between the ion source and the biased probe and the limited transport paths between. The numerical model we developed qualitatively captured such growth and gave a good estimate of growth rate obtained experimentally. A three-probe configuration was used to demonstrate the application of observed silver wire growth to constructing resistive switching device and an equivalent circuit model was proposed to explain the observed electrical current. The fast reversible silver wire growth observed here has potential in applications for electronic devices as well as plasmonic sensors and waveguides.

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