Solid State Electrochemical Nanopatterning
on ionically conducting RbAg4I5 Electrolyte
using AFM Probe

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Scanning probe microscopy (SPM) has been widely investigated and explored for nanolithography [1-7]. Here, we report a new nanolithography technique that is based on fast ion conducting solid electrolyte membranes and is capable of generating topological patterns by electrodeposition of a metal cluster on the surface of the ionically selective membrane.

This novel nanopatterning technique can easily be performed under ambient conditions without involving a liquid vessel or probe-to-sample material transfer. Patterning involves the use of an atomic force microscopy (AFM) probe on the surface of the solid ionic conductor $RbAg_4I_5$. Application of negative voltage pulses on the probe relative to an Ag film counter electrode on the backside of a $RbAg_4I_5$ layer induces nanometer sized Ag clusters to deposit on the ion conductor around the probe tip. (See Figure 1) The patterned Ag particles are 0.5-70nm high and 20-700nm in diameter. Figure 2 shows positive ((a), (b) and (e)) and negative ((c) and (d)) patterns made from sequences of dots generated by applying bias voltage pulses of 200-400mV for 0.25-5ms.

While we demonstrate this new technique on $RbAg_4I_5$, it should also be applicable to a number of other solid ion conductor systems. Compared to some of the previous nanolithography processes, this novel technique exhibits an intriguing operational simplicity because localized patterning is directed only by the straightforward application of electrical bias pulses through a probe tip. Due to the swiftness of this process in generating patterns and the size of the resulting features, it also is ideally suited for erasable high-density data storage applications.

References
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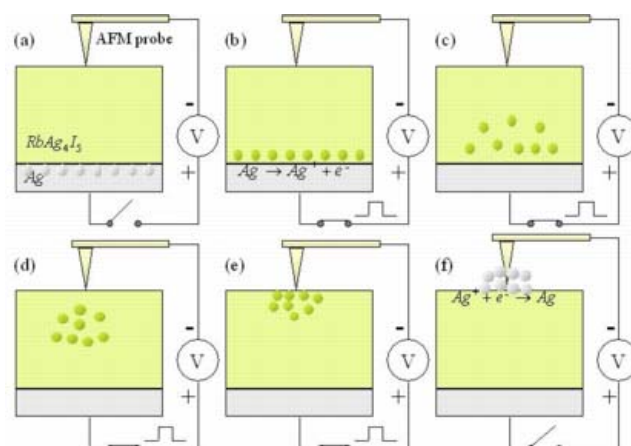**Figure.1:** Simplified schematic diagram of the experimental setup for nanopatterning of Ag on $RbAg_4I_5$, which shows the time evolution of Ag atoms and ions under the voltage bias. Oxidation and reduction processes are depicted in steps (b) and (f) respectively. The migration of silver ions in the ion conductor under the electric field is shown in steps between (b) and (e). Drawing not to scale.
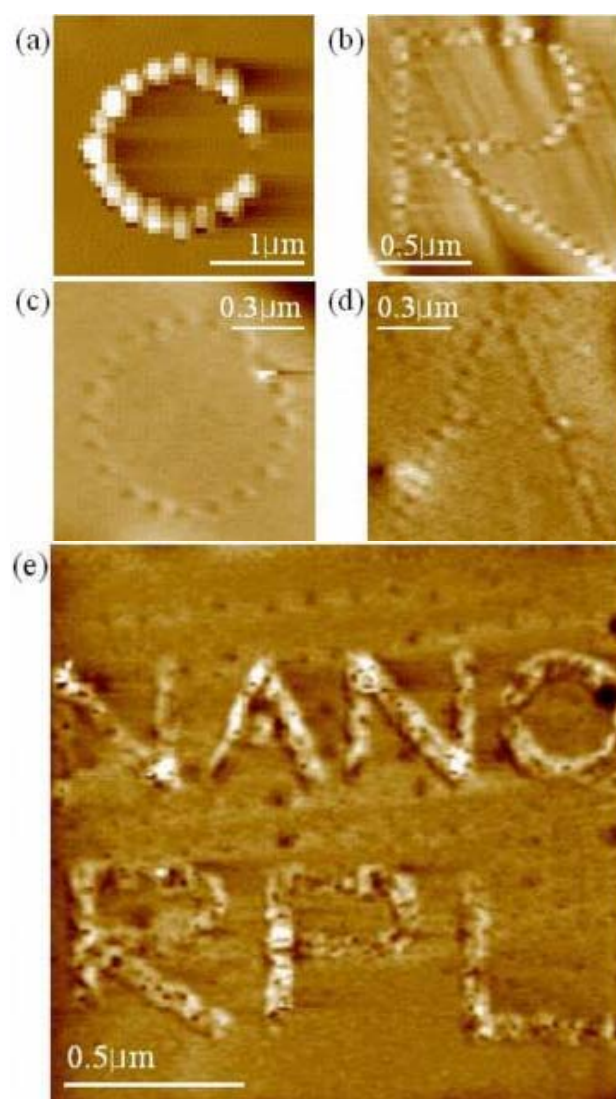

Figure.2: AFM contact-mode deflection picture of electrochemically induced Ag nano-features on RbAg4I5. (a) Positive features generated by 200mV, 5ms pulses for each dot. (b) Positive features generated by 400mV, 1ms pulses (c) Negative features generated by 200mV, 1ms pulses (d) Negative features generated by 200mV, 1ms pulses (e) Positive features generated by 200mV, 0.3ms pulses.