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Supporting Information

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Nonvolatile Electrochemical Random-Access Memory under Short Circuit

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Diana Kim[1,2], Virgil Watkins[1], Laszlo Cline[1], Jingxian Li[1], Kai Sun[1],
Joshua D. Sugar[3], Elliot J. Fuller[3], A. Alec Talin[3], Yiyang Li[1#]

[1]Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA

[2]Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI, USA

[3] Sandia National Laboratories, Livermore, CA, USA

#Corresponding author: yiyangli@umich.edu

Supporting Note 1

ECRAM is a recently developed analog memory that share some mechanisms as a solid-state battery. ECRAM contains three terminals, often referred to as “gate,” “source,” and “drain” based on its geometry, and used to apply voltages and currents. The active components include two mixed ionic and electronic conductors (e.g. WO_{3-X}) that sandwich a solid electrolyte (e.g. YSZ), as shown schematically in Fig. 1a. The two “source” and “drain” electrodes are used to “read” the electronic resistance of the WO_{3-X} channel by applying a small voltage pulse, typically <0.1 V, and measuring the electronic current. The electronic resistance of the channel is controlled by the concentration of ions, which are electron-donating oxygen vacancies in our device. The defect reaction is given in equation 1. A mixed conductor will conduct electrons and ions because it must contain both electrons and oxygen vacancies.

$$2\,O_O^X \rightarrow 2e^- + V_O^{\cdot\cdot} + \frac{1}{2}O_{2(g)} \qquad (1)$$

Switching the resistance state requires changing the ion concentration of the channel, which is realized by applying an electrochemical current through the “gate” terminal using the “write” voltage. Upon the application of an electrochemical voltage, negatively charged electrons move between the switching layer and channel via the external circuit; at the same time, positively charged oxygen vacancy ions move in the same direction through the electrolyte to conserve charge. This results in a change in the oxygen vacancy concentration, which yields a change in the electronic resistance.

A critical component to ECRAM functionality is the solid electrolyte’s ability to conduct ions but block electrons. In YSZ, this is achieved by the substitution of ~15% of the Zr sites with Y, which has one fewer proton than Zr. This yields the defect reaction in equation (2), where the introduction of one Y_2O_3 molecule results in the creation of two ZrO_2 sites in this cubic fluorite material (Supporting Fig. S8).

$$Y_2O_3 \rightarrow 2\,Y_{Zr}' + 3\,O_O + V_O^{\cdot\cdot} \qquad (2)$$

Because this defect reaction creates an oxygen vacancy, YSZ is ionically conducting. However, no mobile electrons are created, in contrast to the mixed conductor in equation 1. Instead, the electrons donated by the oxygen vacancies reside on the Y site, where they are immobile. In other words, because Y has a lower nuclear charge than Zr, it effectively acts as a hole donor. The holes donated by Y exactly compensate for the electrons donated by the oxygen vacancy. This behavior enables YSZ to be electronically insulating but ionically conducting.

Although both ECRAM and ReRAM are nonvolatile memories that operate on the basis of oxygen vacancy migration, there are several substantiative differences in terms of functionality and application.

1) ECRAM is a three-terminal device, while ReRAM is a two-terminal device. ECRAM contains separate read and write terminals, like a floating-gate transistor, while ReRAM uses the same read and write terminal.

2) ECRAM contains an electron-insulating solid electrolyte; in our case, we utilize YSZ, an oxygen ion conductor utilizing a vacancy conduction mechanism[1] (supporting Fig. S8). This solid electrolyte blocks electrons and ensures that only ions can pass between the two WO_{3-X} layers. In contrast, ReRAM only contains one or more mixed ionic and electronic conductors[2] (e.g., TaOx, HfOx). These mixed conductors with a defect reaction like equation (1) enable both electron and ion conduction along the vertical direction of the device. ECRAM's use of a solid electrolyte has the following consequences:

    a. Substantial reduction in the write current. Because only ions are allowed to travel through the electrolyte, the write current is much lower, typically on the order of <1 μA even for a macroscopic device like the one in this work, and one that scales proportionally to <1 pA/ μm^2. In contrast, most ReRAM devices require >0.1 mA switching currents, which leads to substantial scaling challenges.
    b. The solid electrolyte enables direct, precise modulation among hundreds of distinct analog states (Fig. 2b). This results because the electrochemical current, which is given by the applied voltage divided by the ionic resistance[3], is proportional to the rate of change of the ion concentration in the channel. This results in highly deterministic and, in many cases, linear switching. In contrast, ReRAM often struggles to switch reliably even among 32 analog states[3].

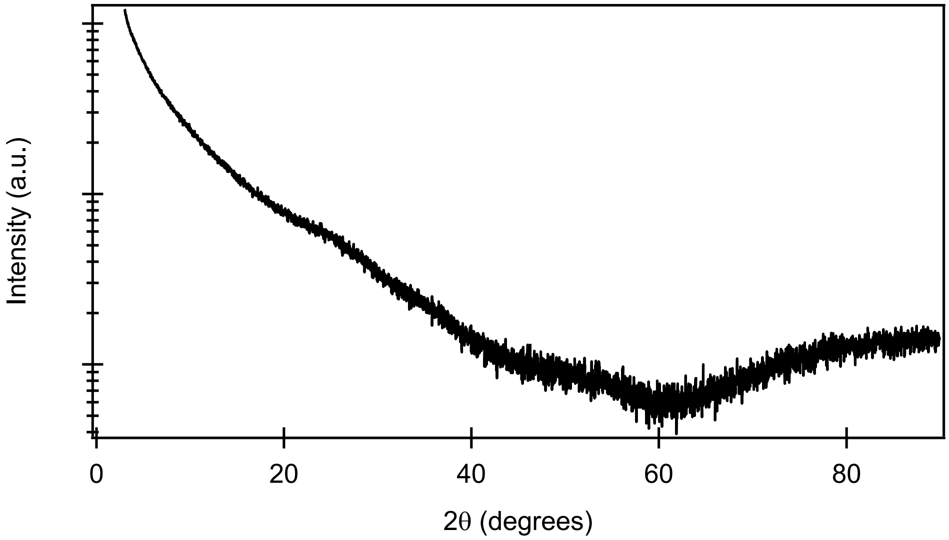
3) The resistance state of ECRAM is controlled using the integrated ionic current, or charge (Q), that passes through the electrolyte. To conserve charge, the ionic charge must equal the integrated electronic charge transferred through the circuit. As shown

in Fig. 3c, there exists a near one-to-one mapping between the integrated charge Q and the conductance G. This charge-controlled mechanism has some similarities to how the measured voltage of a capacitor is controlled by the integrated charge Q.

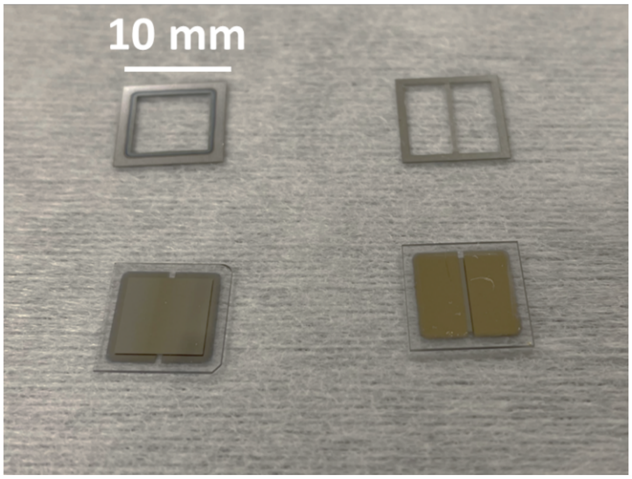
In contrast, the resistance state of ReRAM is controlled by the history of the applied voltage. This history is often dominated by the previous voltage pulse that was applied above the threshold voltage.

4) For these reasons, the three-terminal ERAM is better suited for providing reliable, deterministic, and linear resistance switching among tens or even hundreds of distinguishable resistance states. In contrast, the two-terminal ReRAM is better for simplicity, scaling, and speed. Previously, it was believed that ReRAM has much better retention; however, this work shows that ECRAM can also attain similar retention properties as ReRAM.

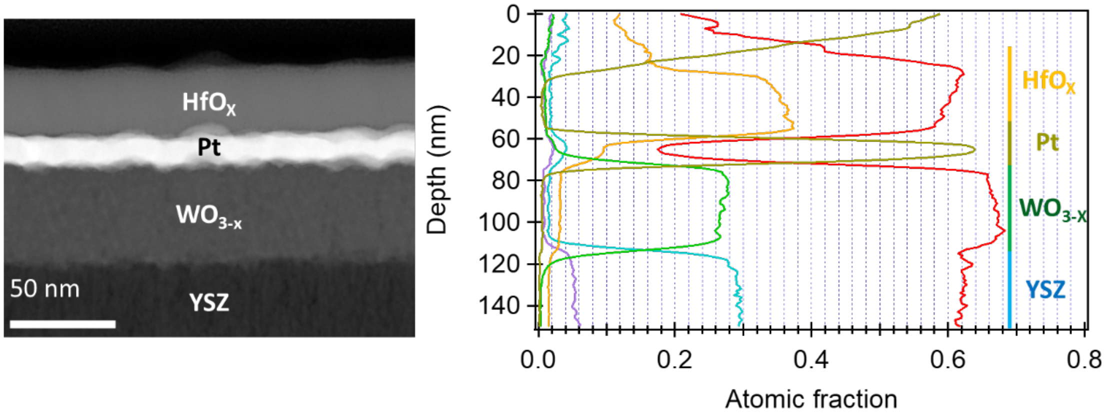
Supporting Figures S1-S8



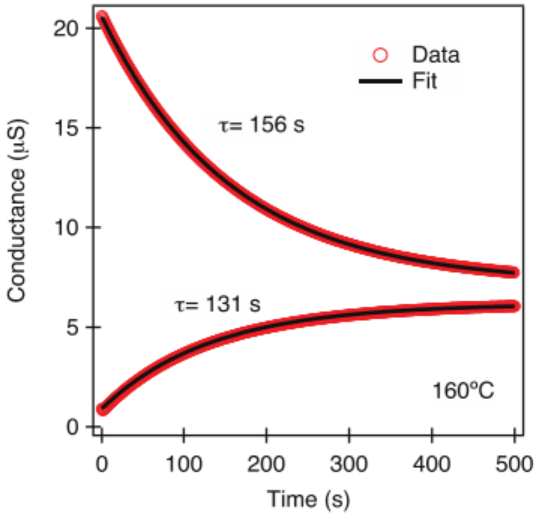
Supporting Fig. S1: X-ray diffraction profile of WO_{3-X} confirms that the channel material is amorphous.



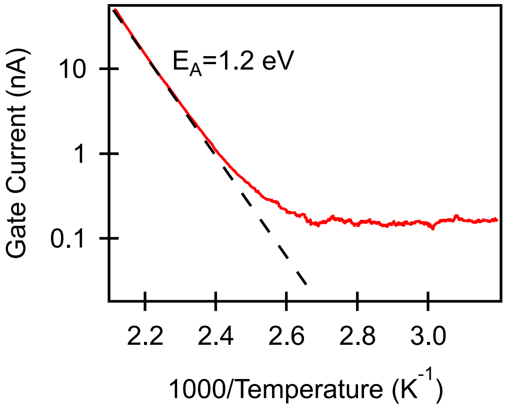
Supporting Fig. S2: Images of the shadow masks and the ECRAM cells used in this study.



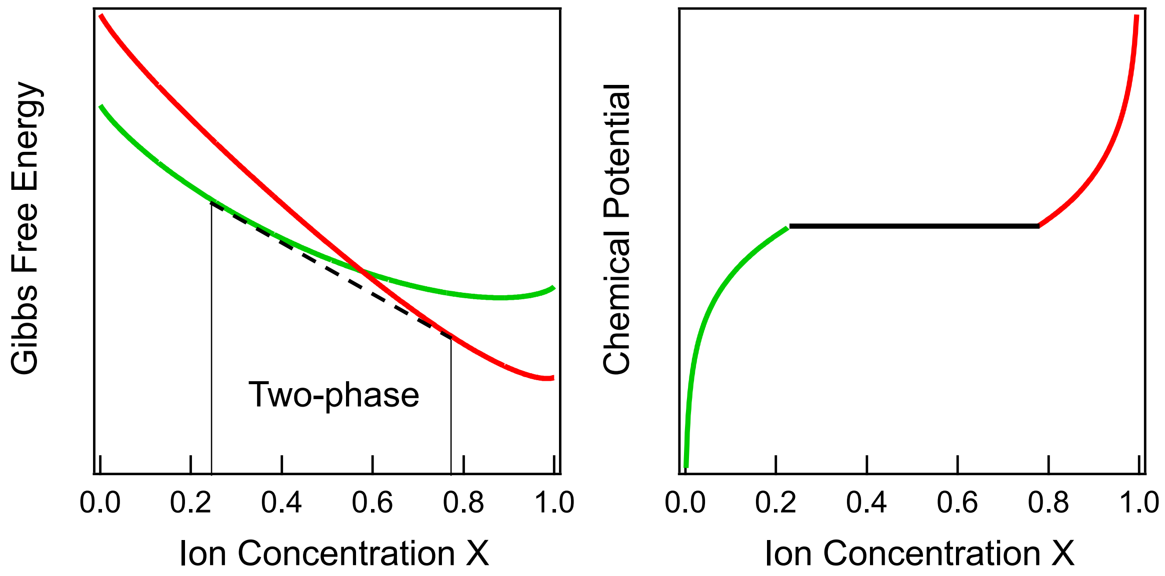
Supporting Fig. S3: STEM and energy dispersive spectroscopy linescan of an ECRAM device shows that the W:O ratio in the WO_{3-X} film is approximately 1:2.5 (X~0.5). Assuming a density of 7 g cm^{-3}, the oxygen vacancy concentration is 8×10^{21} cm^{-3}.



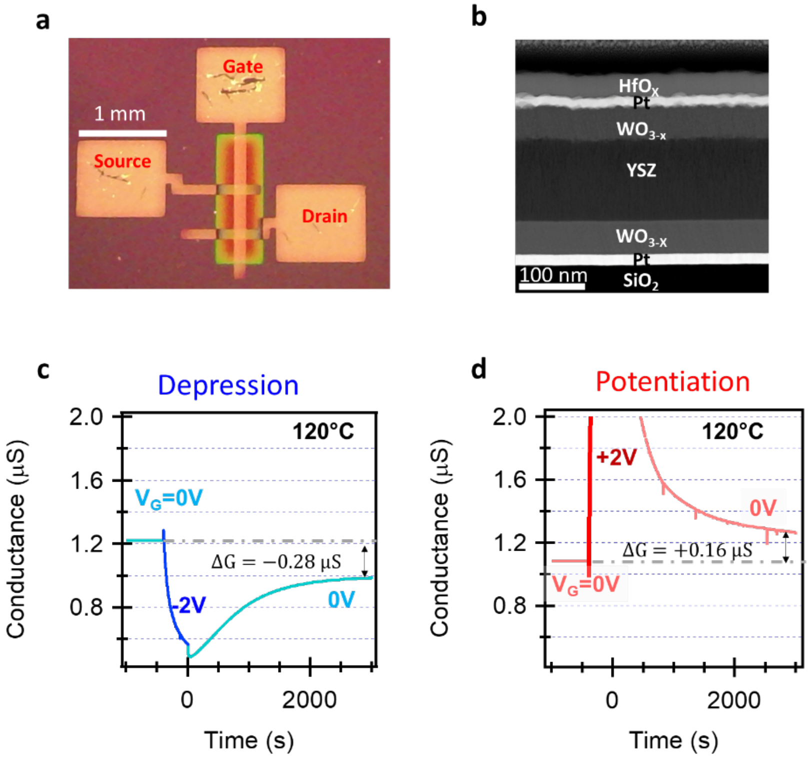
Supporting Fig. S4: Retention behavior of TiO_2-based ECRAM shows rapid convergence to a single value from the high and low resistance state. Data and image from ref. [3].



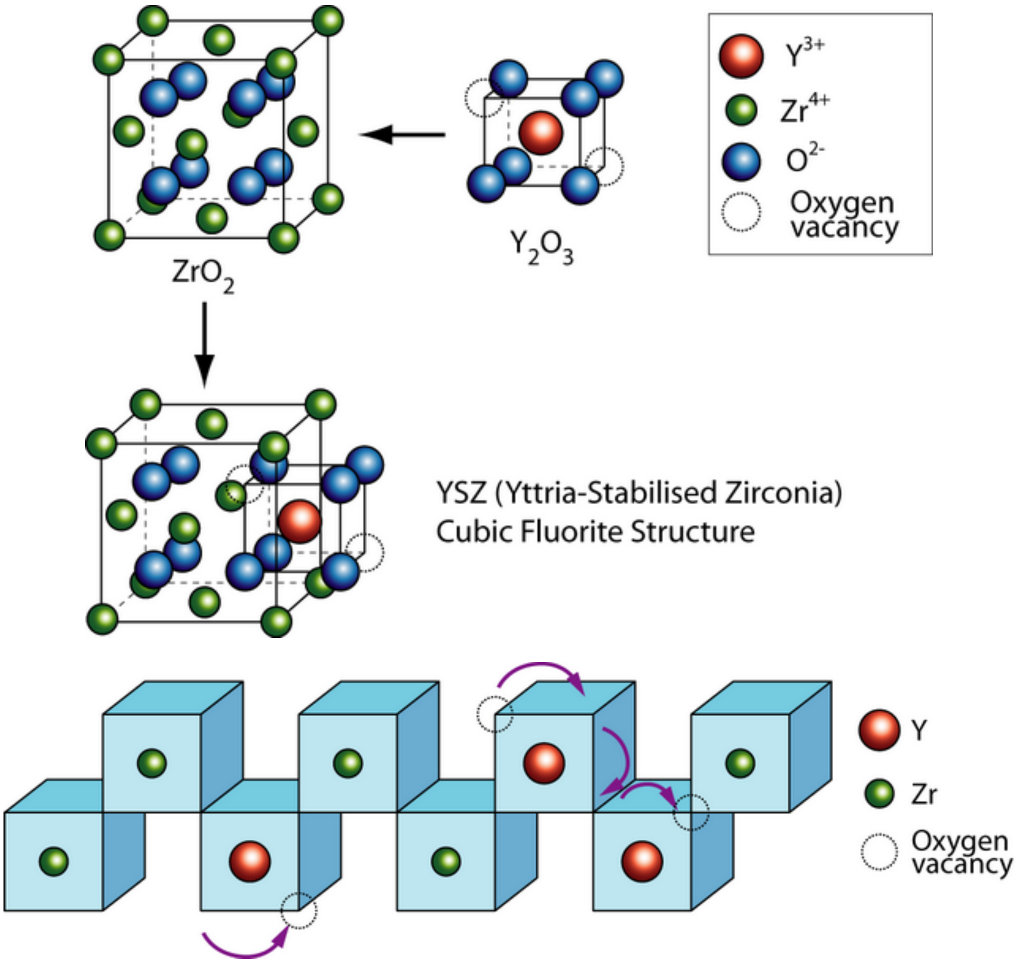
Supporting Fig. S5: The gate electrochemical current upon the application of +2V as a function of temperature shows an Arrhenius relationship with an activation energy of 1.2 eV. This result is consistent with the measured YSZ activation energy of 1.1 eV in previous work. [3]. We note that the currents at lower temperatures is not accurate due to the limitations of the instrument.



Supporting Fig. S6: Phase separation when the common tangent of the Gibbs Free Energy has a lower energy than that of one constituent phase. This common tangent means that the chemical potential, or the slope of the Gibbs Free Energy, is invariant with the ion concentration X.



Supporting Fig. S7: Preliminary demonstration of thin-film ECRAM cell using the same WO_{3-X} gate and channel. (a) Optical micrograph of the thin-film ECRAM. The rectangular region in the middle contains the gate, YSZ electrolyte (deposited by RF sputtering at 100W for a YSZ target and under 3 mtorr of Ar), and channel stacks. (b) Scanning transmission electron microscopy cross-section of the device. (c,d) Potentiation and depression of the cell show some nonvolatile state retention.



Supporting Fig. S8. Schematic illustration of vacancy-drive oxygen ion conduction mechanism of cubic fluorite YSZ. Image reproduced with permission from ref. [4]. Creative common license 2.0 at < https://creativecommons.org/licenses/by-nc-sa/2.0/uk/>

References:

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