## Supplementary Information

# Ultrafast Triggered Transient Energy Storage by Atomic Layer Deposition into Porous Silicon for Integrated Transient Electronics

*by Anna Douglas*<sup>1</sup>, *Nitin Muralidharan*<sup>1</sup>, *Rachel Carter*<sup>2</sup>, *Keith Share*<sup>1</sup>, *and Cary L. Pint*<sup>1,2,3,\*</sup>

<sup>^</sup>Equal contribution first author

<sup>1</sup>Interdisciplinary Materials Science Program, Vanderbilt University, Nashville, TN 37235

<sup>2</sup>Department of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235

<sup>3</sup>Vanderbilt Institute of Nanoscale Science and Engineering, Nashville, TN 37235

### **Experimental Details:**

#### **Etching of porous Silicon**

Preparation of porous silicon was carried using electrochemical etching technique. Highly p-doped porous silicon wafers (0.01-0.02  $\Omega$ /cm) were etched using an AMMT wafer-scale silicon etching system in a 3:8 v/v hydrofluoric acid and ethanol. An etching current of 45 mA/cm<sup>2</sup> was applied for 180 seconds on the silicon wafer to obtain a 5  $\mu$ m deep porous layer. In general, depth of the porous structure can be tailored varying the etching time and etching current. Further optimization of these parameters can enable selective control of pore morphology tuned selectively to obtain desired coatings as well as good device performance

#### VO<sub>x</sub> deposition using ALD

Vanadium oxide (VO<sub>x</sub>) was coated on the obtained porous silicon structure using a GemStar 6" ALD system. The precursor, (98+%) Vanadium(V)tri-i-propoxy oxide (VTIP) with a chemical formula, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> was preheated to 55 °C before the process. Nanopure water (H<sub>2</sub>O) obtained using a Millipore water purifier was used as the oxidizer. The precursor and the oxidizer manifolds were heated to 115 °C to prevent condensation effects. Ultra-high pure Argon was used as the carrier gas and a reaction temperature of 150 °C was maintained throughout the process. To obtain the gradient in thickness of VO<sub>x</sub> coating on the 3D of porous silicon from pore tip to pore depth, VTIP and water pulses of 2 seconds each and short residence times of 2 seconds for both reactants in the reaction chamber was employed. Based on previous reports, residence times of about 20 seconds or greater is required for complete saturation of VTIP and water can be split into two half reactions.

$$(V-OH)_{surface} + VO(OC_{3}H_{7})_{3} \rightarrow (O-V-(OC_{3}H_{7}))_{surface} + HOC_{3}H_{7}$$
(1)  
$$(V-(OC_{3}H_{7}))_{surface} + H_{2}O \rightarrow (V-OH)_{surface} + HOC_{3}H_{7}$$
(2)

Gradient coatings on 3D porous structures using ALD can be generated using this concept which proves beneficial in the immediate disabling of the transient device. To

determine the mass of the  $VO_x$  deposited per cycle, a silicon wafer (Diameter: 100 mm) was etched under the aforementioned conditions and subjected to 500 ALD cycles of  $VO_x$  deposition. The mass of the wafer before and after the ALD process gives an estimation of the mass of  $VO_x$  deposited per cycle on the porous structure.

Ellipsometry for film thickness evaluation



**Figure S1.** Plot of VOx coating thickness as a function of the total number of ALD cycles showing the expected overall linear increase in thickness expected for ALD processes. Thickness estimation of the VO<sub>x</sub> coatings after the ALD process was performed using a JA Woollam M2000VI Spectroscopic Ellipsometer. The measurements were performed on a silicon wafer with VO<sub>x</sub> depositions for various ALD cycles (50-500) using the same process conditions followed in the deposition process of VO<sub>x</sub> on porous silicon.

#### Preparation of the gel electrolyte

3g of poly(vinyl alcohol) (PVA) was dissolved in 30ml of water and 0.5M  $LiClO_4$  was added to the solution under constant stirring at 80 °C. This solution was cooled to room temperature to obtain the consistency of a gel. A freshly prepared gel electrolyte was used as the electrolyte for the transient device.

#### **Preparation of the separator**

5g of poly(ethylene oxide) (PEO) was dissolved in 8g of propylene carbonate containing  $0.5M \text{ LiClO}_4$  was stirred overnight at 60 °C. The viscous solution was then doctor bladed onto a glass slide followed by drying in a vacuum over at 60°C. The film was then peeled off and used as the separator for the transient device.

#### **Electrochemical measurements**

Electrochemical measurements were performed in a symmetric two-electrode configuration with identical electrodes of similar geometrical area. The PEO/LiClO<sub>4</sub> separator with the PVA/LiClO<sub>4</sub> electrolyte was sandwiched between the two VO<sub>x</sub> coated porous silicon electrodes. Cyclic voltammetry (CV) technique was used to analyze the redox behavior of the electrochemically active VO<sub>x</sub> coating between -0.6 V to 0.6 V at a scan rate of 100 mV/s. 19 nm thick VO<sub>x</sub> coated porous silicon corresponding to 400 ALD cycles which showed a reversible redox behavior was cycled at 100 mV/s using CV technique to understand the stability of the redox couple. Galvanostatic charge discharge (CD) analysis was performed at on all samples a current density of 0.1 mA/cm<sup>2</sup> to evaluate the performance of these transient devices. In a symmetric two electrode configuration both the electrodes contribute to the total capacitance of the device. Specific capacitance of these devices in the symmetric two electrode configuration was estimated from the average slope of the discharge curves according to:

$$C_{electrode} = 2C_{cell} = \left(\frac{2I}{\left(\frac{dV}{dt}\right)m}\right)_{,}$$

where m is the mass of the active material on both electrodes, dV/dt is the average slope of the discharge curve and I is the total discharging current. All electrochemical data was normalized to the area of the electrodes tested.



**Figure S2.** TEM image of  $VO_x$  coatings on porous silicon. As labeled, the porous silicon material is darker than the  $VO_x$  in bright field images. TEM images are acquired using an FEI Osiris TEM at a beam voltage of 200 kV and a screen current of 1.3 nA.



**Figure S3.** Raman spectroscopic analysis of the VO<sub>x</sub> material before and after annealing at 450°C in air, with stretch modes labeled. Prior to annealing, broad spectral features, such as the peak centered at 900 cm<sup>-1</sup>, elucidate the presence of a state of VO<sub>x</sub> that is disordered or amorphous. After annealing, the distinct Raman characteristics of V<sub>2</sub>O<sub>5</sub> emerge, indicating the crystallization to the orthorhombic crystalline phase of V<sub>2</sub>O<sub>5</sub>. Raman modes at 283 cm<sup>-1</sup>, 404 cm<sup>-1</sup>, 1006 cm<sup>-1</sup> correspond to the V=O bond and the modes at 304 cm<sup>-1</sup> and 529 cm<sup>-1</sup> indicate the presence of V<sub>3</sub>-O bonds. The Raman modes corresponding to the V-O-V bonds are located around 481 cm<sup>-1</sup> and 710 cm<sup>-1</sup>.<sup>1</sup> In turn, this implies, in correlation with EDS measurements, that the VO<sub>x</sub> material is an oxygendeficient and non-crystalline form of a material related to V<sub>2</sub>O<sub>5</sub>.



**Figure S4.** Cross section SEM image of a porous silicon material with  $VO_x$  distributed uniformly across the length, as opposed to a gradient distribution as described in the main text. Uniform ALD coatings of  $VO_x$  were achieved by doubling the residence time of the precursors in the reaction chamber. The resulting sample was tested to understand the transient behavior from the uniform coating. Images from the dissolution test are shown in Figure S5 (below).



**Figure S5.** Transience of gradient coated  $VO_x$ /porous silicon energy storage electrodes in different triggering solutions (A, B) and uniformly coated VOx/porous silicon electrodes in 1 M NaOH triggering solutions. From A-B, as the pH decreases, the rapid triggering effect is evident based on the detachment of the active material from the silicon electrode, even though the time required to achieve full dissolution is significantly increased – especially for 0.01 M NaOH which takes up to 76 hours to fully dissolve. In contrast to this mechanism, uniformly coated  $VO_x$ /porous silicon transient electrodes do not exhibit the rapid deactivation step observed in the gradient coated electrodes, and fully dissolve while retaining their on-chip configuration in a period of 2 hours. This demonstrates the nature of the gradient ALD coating of  $VO_x$  in allowing ultrafast deactivation that can be useful in transient systems.



**Figure S6.** (A) Electrochemical Impedance Spectroscopy of the 19 nm  $VO_x$  coated porous silicon electrode and (B) Equivalent circuit representation that describes the EIS spectra of 19 nm  $VO_x$  coated porous silicon.

Electrochemical Impedance Spectroscopy was performed on the 19 nm VO<sub>x</sub> coated porous silicon. The symmetric electrode system was subjected to a DC bias of 0 V at an amplitude 10 mV RMS in the frequency range of 100 kHz to 0.01 Hz. The resulting Nyquist plot comprising of the real and imaginary impedances is given in Figure S6A. The VO<sub>x</sub> coated porous silicon has a relatively low ESR value (20  $\Omega$ ) which is evident from the Nyquist curve. Equivalent circuit representing the resistances observed in the system arising from various interfaces is shown in Figure S6B. The polymer electrolyte gel and VO<sub>x</sub> interface, the interface of VO<sub>x</sub> and porous silicon and the interface of porous silicon and the electrolyte resulting from the gradient coating of VO<sub>x</sub> comprise the resistances in this system. As the measurements were performed in a symmetric two electrode configuration, the resistance corresponding to the VO<sub>x</sub> electrolyte interface has a moderate value of about 170  $\Omega$ .



**Figure S7.** Representative Energy Dispersive X-Ray Spectroscopy cross-sectional spectrum of  $VO_x$  coated porous silicon electrode. The EDS spectrum shows elements of Vanadium, Oxygen, Silicon, and Carbon (from the carbon tape substrate). Based on compositional analysis of the vanadium oxide material, assumed to only contain V and O, this indicates relative weight percentage of Vanadium and Oxygen as 64% Vanadium and 36% Oxygen within the VO<sub>x</sub> composite.