## Electron beam induced local crystallization of HfO<sub>2</sub> nanopores for biosensing applications

## **Supplementary Information**

Jiwook Shim<sup>1, 2, 3#</sup>, Jose Rivera<sup>1, 3#</sup> and Rashid Bashir<sup>1, 2, 3</sup>\*

<sup>1</sup>Department of Bioengineering, <sup>2</sup>Electrical and Computer Engineering, and

<sup>3</sup>Micro and Nanotechnology Laboratory, University of Illinois at Urbana – Champaign, Urbana, IL 61801

<sup>#</sup> Authors contributed equally

\* Corresponding Author: rbashir@illinois.edu

Rashid Bashir, PhD Abel Bliss Professor, Department of Bioengineering, Department of Electrical and Computer Engineering Director, Micro and Nanotechnology Laboratory University of Illinois at Urbana – Champaign, Urbana, IL 61801, USA Figure S1.



Figure S1. TEM images and corresponding FFT images of nanopores on SiNx membrane and HfO2 membrane. SiN membrane (Protochips, NC) is free-standing 30 nm-thick membrane over 50  $\mu$ m × 50  $\mu$ m window. Membrane thickness was reduced to 16 nm by HF etching. TEM image of a nanopore in SiN (top-left) was taken immediately after drilling using focused electron beam. Nanopore drilling process does not alter the characteristic of SiN membrane to crystallization phase, and FFT (bottom-left) image confirmed that SiN remained as amorphous membrane. A nanopore in as-deposited HfO2 membrane (top-right) was taken after nanopore drilling. Crystallization pattern was observed at nanopore region and corresponding FFT (bottom-right) image showed crystallization pattern as well. Scale bars in TEM images are in 2nm.

Figure S2.



**Figure S2. The interface leakage current.** The leakage through interface between the graphene/TiO<sub>2</sub> and HfO<sub>2</sub> increases with applied bias for the as-deposited film to 2.5nA/mm<sup>2</sup> at 500mV, and for the crystallized film to  $\sim 1.75$ nA/mm<sup>2</sup> at -500mV and greater than 200 nA at 500mV, indicating increased degradation of the insulator after crystallization. Non-uniform coverage of the dielectric, pinholes, and graphene wrinkles<sup>1, 2</sup> can result in greater leakage density and lower dielectric breakdown for HfO<sub>2</sub> on graphene when compared to a bare silicon substrate. However, the high-k HfO<sub>2</sub> based architecture allows for future studies where leakage can be mitigated by increasing dielectric thickness without sacrificing the large gate capacitance density of HfO<sub>2</sub>.

## Figure S3.



**Figure S3. Contact angle measurement of Si3N4 membrane.** Four contact angle measurement of SiN membrane are shown here. We have measured contact angle at  $74.7^{\circ} \pm 1.06^{\circ}$  from five different membranes.





**Figure S3. Histograms with fitting of current blocking and translocation duration.** Current blocking and translocation duration histograms were constructed with all events at 300mV and 400mV. The value of current blocking was obtained fitting to Gaussian function and the value of translocation duration was by exponential function.

- 1. Merchant, C.A. et al. DNA Translocation through Graphene Nanopores. *Nano Lett* **10**, 2915-2921 (2010).
- 2. Banerjee, S. et al. Electrochemistry at the Edge of a Single Graphene Layer in a Nanopore. ACS Nano 7, 834-843 (2013).