DOI: 10.1002/ ((please add manuscript number))

Article type: Communication

Integration of Electrochemical Microsupercapacitors with Thin Film Electronics for On-Chip Energy Storage

Mrinal K. Hota¹, Qiu Jiang¹, Zhenwei Wang¹, Zhong Lin Wang³, Khaled N. Salama^{2}, and Husam N. Alshareef^{1,*}*

Dr. M. K. Hota, Mr. Q. Jiang, Dr. Z. Wang, and Prof. H. N. Alshareef *

¹Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
*E-mail: husam.alshareef@kaust.edu.sa

Prof. K. N. Salama*

²Sensors lab, Advanced Membranes, and Porous Materials Center, Computer, Electrical, and Mathematical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
*E-mail: khaled.salama@kaust.edu.sa

Prof. Z. L. Wang

³School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

Keywords: on-chip energy storage; thin film transistor; thin film diode; micro-supercapacitor; RuO₂

Abstract

The development of self-powered electronic systems requires integration of on-chip energy storage units to interface with various types of energy harvesters, which are intermittent by nature. Most studies have involved on-chip electrochemical microsupercapacitors that have been interfaced with energy harvesters through bulky Si-based rectifiers that are difficult to integrate.

In this study, we demonstrate transistor level integration of electrochemical microsupercapacitors and thin film transistor rectifiers for the first time. In our approach, the thin film transistors, thin film rectifiers, and microsupercapacitors share the same electrode material for all, which allows for a highly integrated electrochemical on-chip storage solution. The thin film rectifiers are shown to be capable of rectifying ac signal input from either triboelectric nanogenerators or standard function generators. In addition, electrochemical microsupercapacitors exhibit exceptionally slow self-discharge rate (~ 18.75 mV/hour) and sufficient power to drive various electronic devices. This study opens a new avenue for developing compact on-chip electrochemical micropower units integrated with thin film electronics.

In recent years, autonomous and self-powered electronic devices started playing an increasingly important role especially in applications such as wearable electronic devices, epidermal electronic sensors, and sensors for the internet of things (IoT).^[1-4] This gave rise to a range of energy harvesting technologies such as piezoelectric, triboelectric, thermoelectric micropower generators. These energy harvesting approaches are all intermittent by nature. Hence, self-powered devices require the integration of on-chip energy storage unit to work in tandem with the energy harvester.^[5,6] However, conventional batteries lack the necessary cycle life and cannot deliver the required high power for applications where battery replacement may not be practical (*e.g.*, implantable medical biosensors, remote sensors, sensors for structural health monitoring, and IoT sensors). In contrast, microsupercapacitors (MSCs) have very long cycle life, fast charging rates, and high-power density.^[7-12] In addition, by drawing the maximum current that the source can supply, MSCs charge more efficiently compared to thin film batteries,

making supercapacitors more suitable for self-powered system applications in which the harvester-generated voltage may be variable.^[13]

In order to store energy from such intermittent harvesters, the ac signal must first be rectified before being stored in an electrochemical capacitor. Many publications on self-powered devices use off-the-shelf bulky rectifiers at the interface between the nanogenerator ac signal and a storage capacitor.^[14,15] These rectifiers, which are made using conventional silicon-based p-n or Schottky junction diodes, are bulky as they are packaged inside IC chip carriers, which makes miniaturization of the nanogenerator-electrochemical supercapacitor system challenging. It is therefore important to replace these bulky rectifiers with rectifiers fabricated using thin film electronics technology integrated on the same chip with electrochemical capacitors.

In this work, we propose a new approach to integrate electrochemical micro-supercapacitors on-chip with thin film transistors and rectifiers to fabricate a highly integrated monolith rectifier-storage unit. A unique aspect of this work is that we use the same material for both transistor gate electrodes and microsupercapacitor electrodes, which significantly simplifies the fabrication process leading to easy integration with nanogenerator and sensor. The integrated microsupercapacitor-thin film rectifier system performance is demonstrated using signals generated from triboelectric nanogenerators as well as function generators. The performance of the microsupercapacitors, thin film transistor rectifiers, and integrated system show that it is a promising approach for self-power system applications.

Figure 1a shows a schematic illustration of our device concept. The unit consists of microsupercapacitor (**Figure 1b**) fabricated using a total of 30 fingers of length 2350 μm each that have 100 μm width each and 50 μm spacings between them having a total surface area of 0.096 cm^2 . The rectifier circuits (**Figure 1c**) were fabricated on the same substrate. By using

RuO₂ as a common electrode material for both the microsupercapacitors and transistor electrodes, a compact rectifier-electrochemical supercapacitor device was fabricated as shown in **Figure 1d**. The schematic of the device process flow is illustrated in **Figure S1a** (see *Supporting Information Section*).

RuO₂ was selected as electrode material for both thin film transistors and electrochemical supercapacitors for several reasons: (1) it is a well-known pseudocapacitive electrode material (2) it exhibits metallic conductivity, which is an important characteristic for microsupercapacitors and transistor electrode materials, (3) it has good cycling stability, and (4) our RuO₂ process shows a very good self-discharge characteristics, when processed with the appropriate microstructure, as we show later.

Different RuO₂ thin films were prepared on glass substrates at room temperature by reactive magnetron sputtering in a gas mixture of Ar and O₂ using a ruthenium metal target. The electrical resistivity of different RuO₂ thin films was studied using four-probe measurements as a function of oxygen partial pressure (O_{pp}) and RF power. It was found that the resistivity increases with increasing O_{pp} (**Figure 2a**) but decreases with increasing deposition RF power (**Figure S2a**). Film crystallinity was found to improve with RF power, leading to a more ordered film and hence resistivity decreases.^[16] It should be noted, however, that the resistivity values are found to be comparable to previously reported resistivity values of sputtered RuO₂.^[17]

The crystallinity of RuO₂ thin films deposited on glass substrates was investigated using X-Ray diffraction, as shown in **Figure 2b**. The major crystalline peak corresponding to (110) planes of RuO₂ is present at $2\theta=28^\circ$ for all samples. It is noticeable that the peak becomes broad for RuO₂ films deposited at higher O_{pp} . Another broad peak was found at 55° corresponding to the (211) planes for the samples deposited using more than 20% O_{pp} . These peaks are consistent

with the rutile crystal structure of RuO_2 .^[18,19] The RuO_2 thin films are further characterized by Raman spectroscopy (**Figure 2c**), which shows three major Raman vibration modes, including E_g , A_{1g} , and B_{2g} located at ~ 505 , 621 and 685 cm^{-1} , respectively. The E_g and A_{1g} peaks are found to be broad with a redshift at higher O_{pp} , indicating less ordered films.^[20,21] The XRD and Raman shifts obtained from pure Ru ($0\text{ }O_{pp}$) were also studied as a reference, and are shown in **Figure S2b** and **Figure S2c**, respectively.

The chemical compositions of different RuO_2 thin films were analyzed using X-ray photoelectron spectroscopy (XPS), as shown in **Figure 2d**. It can be observed that the XPS spectrum for Ru $3p$ is a doublet, with $3p_{3/2}$ and $3p_{1/2}$ observed at lower and higher binding energies, respectively. The thin films show no metallic Ru, rather they are fully oxidized and peak fitted to four components. The main intense peaks at 462.7 and 484.9 eV are attributed to Ru^{4+} (shown as region “I” in **Figure 2d**).^[22] The three small peaks at higher binding energy are attributed to absorbed moisture: $\text{RuO}_x \cdot y\text{H}_2\text{O}$ (at 464.8 and 486.9 eV (region “II”), Ru^{6+} of RuO_3 (at 466.3 and 488.6 eV (region “III”) and Ru^{8+} of RuO_4 (at 468.1 and 490.3 eV (region “IV”).^[23,24] It was noticed that the peaks shift slightly towards higher binding energies with increasing O_{pp} values. Also, from the XPS curve fitting results, it was found that the amount of $\text{RuO}_x \cdot y\text{H}_2\text{O}$ increases with increasing O_{pp} . For example, about 8% higher $\text{RuO}_x \cdot y\text{H}_2\text{O}$ was observed for RuO_2 films deposited at 28% O_{pp} as compared to 8% O_{pp} RuO_2 films. The surface morphology of the RuO_2 thin film deposited under 28% O_{pp} was inspected using atomic force microscopy and is shown in **Figure 2e**. The RMS value of roughness was found to be 1.95 nm for the 250 nm thin film on a glass substrate. **Figure 2f** shows a high-resolution cross-section dark field scanning transmission electron microscope (STEM) image of a typical multi-layer

stack used to fabricate rectifiers in this study. All layers can be clearly identified with relatively sharp interfaces, which illustrates the uniform deposition process of the different layers.

TFTs were developed and used to fabricate on-chip rectifiers which were subsequently integrated with the electrochemical microsupercapacitors. Our goal was to make thin film transistors in the bottom gate configuration, wherein the transistor gate material (RuO_2) is the same material used for the electrochemical microsupercapacitor electrodes. A typical structure of our TFTs is shown in **Figure S4**. From our previous report,^[25] we know that ZnO (~25 nm) as a channel layer and HfO_2 (~130 nm) as a gate dielectric can give good TFT performance and hence we started our study considering these facts. Notice that the gate material is made with RuO_2 , which is the first report on ZnO based TFTs using RuO_2 as gate electrodes. The output and transfer curves obtained from a typical TFT are shown in **Figure 3a** and **Figure 3b** respectively. It can be seen that the output curves show good saturation with no hysteresis in the transfer characteristic curves. The fabricated TFTs show high $I_{\text{on}}/I_{\text{off}}$ ratio of $>10^8$, a subthreshold swing of $\sim 791 \text{ mV dec}^{-1}$ and high saturation mobility (μ_{Sat}) of $\sim 12.82 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with a turn-ON voltage of -2.13 V. The TFT performance obtained with RuO_2 as a gate electrode is comparable to ZnO based TFTs reported in the literature.

Thin film transistor rectifiers (TFTR) are designed and fabricated in this study by shorting the gate to drain terminals of the transistor; in this way, the device operates only in saturation region following the relationship: $V_{\text{in}} > V_{\text{Dsat}} + V_{\text{th}} > V_{\text{ON}}$. Hence, the gate to drain short terminal act as an anode (input terminal) of the TFTR and the source terminal act as a cathode (output terminal). Therefore, during the application of the positive bias to the anode, charge accumulation in the channel/gate dielectric occurs due to electric field effect and, as a result, the diode conducts resulting in forward bias configuration just like a conventional diode. The

1 electrons are depleted from the channel/gate dielectric interface under the application of the
 2 negative voltage to the anode terminal. Hence, the TFTR becomes reversed biased which
 3 prevented negative voltages from passing through the diode. By shorting the gate to drain
 4 terminals of the TFTs mentioned above, we obtained a poor dc rectification ratio of $\sim 10^4$ times
 5 only (**Figure 3c**). It can be observed that the forward current of the TFTR at 10V, is comparable
 6 with the ON current of the TFT. However, the reverse biased current of the TFTR is on the order
 7 of $\sim 10^{-8}$, whereas the OFF current of the TFTs is on the order of $\sim 10^{-12}$. We believe that the
 8 negative turn-ON voltage of the TFTs limited it to be fully depleted resulting in high reversed
 9 bias leakage current. We took a strategy to reduce the reverse biased rectifier leakage current by
 10 shifting the turn-ON voltage to higher positive values while keeping the same electron mobility,
 11 and ON current. We shifted turn-ON voltage by reducing the thickness of the channel layer
 12 keeping other layers of the TFTs unchanged. However, beyond a certain thickness of the channel
 13 layer the mobility and the ON current start reduces significantly. Here, we included TFT
 14 performance obtained from the devices with a channel thickness of ~ 20 nm and ~ 14 nm. Good
 15 current saturation was obtained in both devices as shown in **Figure 3d** and **Figure 3g**. Also,
 16 from the transfer curves, it was found that the turn-ON voltage reduces to 0.75 V for the TFT
 17 with a channel thickness of ~ 14 nm (see **Figure 3h**). However, the saturation mobility was
 18 slightly reduced ($\sim 11.96 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), but still acceptable for the rectification operation. Also, an
 19 ON/OFF ratio of $\sim 10^9$ and low SS of 417 mV dec^{-1} were obtained. A good dc rectification ratio
 20 of $\sim 10^7$ times at $\pm 10\text{V}$ was obtained (**Figure 3i**). This rectification ratio is comparable to many p-
 21 n junctions, and Schottky diodes reported elsewhere.^[26-28]

22 For the AC performance of a single stage TFTR, the output signal was captured using an
 23 oscilloscope across a load resistance (**Figure 4a**). **Figure 4b** shows applied input sinusoidal

signals (1 kHz frequency) with a different peak to peak voltage values. The output half wave signals obtained using different external loads including 5.5k, 10k, 46k, 67k, 98k, 110k, and 10 M Ω are shown in **Figure 4c**. It was found that with increasing load resistance, the positive maximum peak voltage increases up to 4.48 V when 110 k Ω resistance was used as an external load. However, the peak voltage decreases to 800 mV with the use of 10 M Ω as an external load. In our remaining study, we used 110 k Ω as the external load.

However, it was found that the output signals contain a smaller voltage amplitude as compared to the input signals (**Figure 4d**), which implies some voltage drop across the TFTR (as the channel has a finite resistance).^[29] With fixing external load (110 k Ω) and peak to peak voltage of 20 V, different input signals with varying frequency were studied to monitor output performance, as shown in **Figure 4e**. It was found that the TFTR performed well in the frequency range of 10 Hz to 30 kHz. At frequencies higher than 30 kHz, the output signal did not follow the input signal well, resulting in poor rectification. Even though the higher cut-off frequency of our TFTRs is smaller than conventional diodes, it is still suitable for many self-powered sensors, where a signal with a frequency range from few Hz to several kHz is required. In context, the TFTR with -2.13 V as turn-ON voltage show ac rectification up to 200 Hz only (see **Figure S6**).

Also, the TFTRs were characterized with the output signal of a homemade triboelectric nanogenerator (TENG). A typical TENG signal which was used as an input signal to the TFTR, and the half-wave rectified signal is shown in **Figure S7**. This result shows that our TFTRs with RuO₂ electrodes can be used to rectify different input ac signals, including those generated by TENGs.

For self-powered systems, microsupercapacitors offer several advantages as integrated micropower sources. We fabricated microsupercapacitors with interdigital electrodes using the same RuO_2 material used for transistor and rectifier contacts to facilitate their on-chip integration. RuO_2 thin films containing higher $\text{RuO}_x \cdot y\text{H}_2\text{O}$ content were used to improve supercapacitor performance.^[30] The electrochemical performance was evaluated using a polymer gel electrolyte (PVA- H_2SO_4) cross-linked with glutaraldehyde (GA). Four gel electrolyte solutions prepared using 0.5, 2.5, 5 and 10 mass% GA respectively were added into PVA- H_2SO_4 solution. The cyclic voltammetry (CV) measurements were performed using these four-gel electrolytes coated on identical RuO_2 microsupercapacitors, as shown in **Figure 5a**. It can be seen that nearly rectangular CV curves with a potential window of 1.0 V were obtained for all devices under a scan rate of 100 mV/Sec. The absence of oxidation and reduction peaks with near rectangular CV shape shows nearly ideal capacitive behavior with excellent reversibility, high rate capability, fast redox reactions at the surfaces of the electrodes. Further, it was found that the area under the CV curve increases with decreasing GA amount. This means that a critical volume of the cross-linking agent is required to achieve good performance, where the gel electrolyte can produce sufficient ions and good quality interface between active electrodes/electrolyte.^[31,32] The solidification of the gels increases dramatically with increasing GA content leading to higher internal resistance. As a result, the electrochemical performance degrades at higher volumes of GA.^[33]

The capacitive behavior was further investigated using galvanostatic charge-discharge (CD) measurements at a fixed current density of $0.1 \text{ mA} \cdot \text{cm}^{-2}$, as shown in **Figure 5b**. All CD curves show near linear and symmetric charge and discharge profiles which suggests an excellent capacitive behavior with a rapid current-voltage response. The highest capacitance

values were obtained for the MSC with 0.5% GA (**Figure 5c**). It should be noted that the areal capacitance values in our RuO₂ based MSCs are small as compared to chemically derived RuO₂ electrode (*e.g.*, Liu *et al.* reported areal capacitance of 40.7 mF/cm² [34]) or even conventional carbon-based MSCs (*e.g.*, L. Kou *et al.* reported areal capacitance of 177 mFcm⁻² in rGO/CNT based supercapacitors[35]). The small capacitance is mainly due to three reasons: (1) lack of sufficient water in the sputtered RuO₂ thin films, as compared to chemically derived RuO₂, which limits protonic conduction in the bulk of the active material;[36] (2) sputtered RuO₂ electrode surface is very smooth, and has almost no pores, which reduces the electrochemically active surface area of the electrodes, (3) thickness of the RuO₂ electrodes is only ~250 nm, which is significantly smaller than thickness of electrodes used in conventional MSCs.[37-40] However, the volumetric capacitance of our microsupercapacitors is still comparable to many reported carbon-based microsupercapacitors. A comparison of the areal and volumetric capacitance of our RuO₂ with several other materials is presented in Table S1 in the *Supporting Information* section.

The effect of RuO₂ electrode thickness on electrochemical properties was also investigated with four different RuO₂ thicknesses (125, 250, 500, and 750 nm). The CV and CD curves are presented in **Figure 5d** and **Figure 5e**, respectively. It can be seen that the areal capacitance increases with RuO₂ thickness, as shown in **Figure 5f**, which can be attributed to the increased electrode surface area exposed to the electrolyte. Further details on the CV and CD curves of MSCs obtained from different gel electrolyte, and RuO₂ thicknesses are shown in **Figure S8** and **Figure S10**, respectively. For the remaining works, we selected 250 nm thick RuO₂ electrodes because they offer a compromise between MSC performance and ease of TFTR fabrication.

1 In practical operation, electronic circuits generate heat. Thus the temperature dependence
2 CV and CD (inset) curves were also studied in the range of 30 to 80 °C (**Figure 5g**), which show
3 a stable electrochemical performance even at a higher temperature, signifying that our devices
4 remain stable during high-temperature operation. A small improvement in both CVs and CDs
5 were noticed with increasing temperature, which is possibly due to improved ionic conductivity
6 at the higher temperature. On the other hand, nearly 95% of the initial capacitance was retained
7 after 10,000 continuous charge/discharge cycles (**Figure 5h**).

8 Another critical aspect of microsupercapacitor performance for self-powered applications
9 is the self-discharge rate of MSCs, which was studied by charging an MSC device to 1V for 40
10 sec, and then monitoring the self-discharge process as shown in the inset of **Figure 5h**. It was
11 found that our MSCs can hold 55% of initial voltage even after 24 hours, with a slow decay rate
12 of ~18.75 mV/hour, which is sufficient for many miniature devices that intermittently measure
13 and transmit signals, where they literally need the power for 10-20 sec. The power output
14 characteristics were studied using Ragone plot, as shown in **Figure S11b**. It can be seen that the
15 energy density decreases with increasing power density. A maximum energy density of 19.21
16 mWh.cm⁻³ was achieved at a power density of 2 W.cm⁻³. In modern implantable and wearable
17 electronic devices, a power supply in the range of 1–100 µW is required.^[41,42] As an example,
18 for modern pacemakers, the required maximum power is only 1 µW.^[43,44] Therefore, the energy
19 consumption for such devices with 1 µW power for 1 hour is about 3600 µJ, which corresponds
20 to a capacitance of ~7.2 mF. However, micropower sources especially for sensing applications
21 are mostly in standby mode, and are only active for seconds to collect data. Thus, the power
22 density of our microsupercapacitors is sufficient to power such devices on an intermittent basis.

On the other hand, while a potential window of 1V was obtained with one MSC, it can be increased to 2V by connecting two MSCs in series (**Figure 5i**).

The on-chip storage performance of the integrated microsupercapacitor-thin film rectifier system is first demonstrated by charging one single MSC using the ac signal from a function generator. The circuit arrangement for this study is shown in **Figure S12**. Before applying any signal to the MSC, the two electrodes were shorted to remove any pre-stored charges (**Figure 6a**, region “I”). Sinusoidal ac signals with different frequencies (a constant peak-to-peak voltage of 20V) were applied to the input terminal of the TFTR, and the output of the TFTR was applied directly to MSC to charge it up to 1V (**Figure 6a**, region “II”). After reaching to 1V, the input signal was shut down, and the stored charge in the form of voltage was monitored for approximately 100 sec (**Figure 6a**, region “III”) before shorting the two MSC electrodes again (**Figure 6a**, region “IV”). It was found that the MSC charging rate is ~34 mV/Sec, which decreases with increasing frequency of the applied input signals (**Figure 6b**). On the other hand, the effect of peak-to-peak voltage of the input signal on MSC charging was also monitored as shown in **Figure 6c**. Different input signals were allowed to charge the MSC through the TFTR for 40 sec and then the input signal was cut off. It was found that the charging rate increases with increasing peak to peak voltage of the applied input signals, as shown in **Figure 6d**. However, it was found that no charging occurs with the application of the input signal of 5V peak to peak voltage, which is not sufficient to charge the MSCs during the allotted time. The optical image of a real on-chip device is shown in **Figure 6e**, next to KAUST logo. Also, we demonstrated in **Figure 6f** that our microsupercapacitors can power up a commercial digital hygro-thermometer.

In summary, we have demonstrated the integration of electrochemical microsupercapacitors and thin film electronics using a single contact material (RuO_2) for both

1 devices. Our thin film rectifiers can replace bulky packaged Si rectifiers that have been typically
2 used in self-powered sensor systems. This can lead to truly on-chip energy storage at the
3 transistor level, which could revolutionize the self-powered sensor by making them more
4 compact and more compatible with standard fabrication methods. In fact, our common electrode
5 material concept can in principle be realized using other electrochemically active materials such
6 as graphene, MXene, and other oxides. The functionality of the integrated electrochemical
7 microsupercapacitor-thin film rectifier system was also successfully demonstrated using
8 triboelectric nanogenerator and ac input signals, which was properly stored, and used to power
9 several electronic devices.

14 **Experimental Section**

15 Experimental details including material deposition, device fabrication and characterizations can
16 be found in the *Supporting Information*.

17 **Supporting Information**

18 Supporting Information is available from the Wiley Online Library or from the author.

20 **Acknowledgements**

21 Research reported in this publication was supported by King Abdullah University of
22 Science and Technology (KAUST). The authors thank the core laboratory and the imaging and
23 characterization staff at KAUST for their support.

1

2

3

4

5

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

1 **Reference**

- 2 [1] I. R. Mineev, P. Musienko, A. Hirsch, Q. Barraud, N. Wenger, E. M. Moraud, J. Gandar, M.
3 Capogrosso, T. Milekovic, L. Asboth, R. F. Torres, N. Vachicouras, Q. Liu, N. Pavlova, S. Duis,
4 A. Larmagnac, J. Vörös, S. Micera, Z. Suo, G. Courtine, S. P. Lacour, *Science* **2015**, 347, 159.
- 5 [2] B. C-K. Tee, C. Wang, R. Allen, Z. Bao, *Nature Nanotech.* **2012**, 7, 825.
- 6 [3] C. R. Merritt, H. T. Nagle, E. Grant, *IEEE Sens. J.* **2009**, 9, 71.
- 7 [4] P-K. Yang, L. Lin, F. Yi, X. Li, K. C. Pradel, Y. Zi, C-I. Wu, J-H. He, Y. Zhang, Z. L. Wang,
8 *Adv. Mater.* **2015**, 27, 3817.
- 9 [5] B. Wang, M. Ahmed, B. Wood, F. Iacopi, *Appl. Phys. Lett.* **2016**, 108, 183903.
- 10 [6] J. Li, V. Mishukova, M. Ostling, *Appl. Phys. Lett.* **2016**, 109, 123901.
- 11 [7] N. Liu, Y. Gao, *Small*, **2017**, 13, 1701989.
- 12 [8] Y. Da, J. Liu, L. Zhou, X. Zhu, X. Chen, L. Fu, *Adv. Mater.* **2018**, 1802793
- 13 [9] D. P. Dubal, N. R. Chodankar, D. H. Kim, P. G. Romero, *Chem. Soc. Rev.* **2018**, 47, 2065.
- 14 [10] P. Zhang, F. Wang, M. Yu, X. Zhuang, X. Feng, *Chem. Soc. Rev.* **2018**, 47, 7426.
- 15 [11] N. A. Kyeremateng, T. Brousse, D. Pech, *Nat Nanotechnol.* **2017**, 12, 7.
- 16 [12] H. Hun, Z. Pei, C. Ye, *Energy Storage Materials* **2015**, 1, 82.
- 17 [13] Q. Jiang, C. Wu, Z. Wang, A. C. Wang, J-H. He, Z. L. Wang, H. N. Alshareef, *Nano Energy*
18 **2018**, 45, 266.
- 19 [14] X. Pu, M. Liu, L. Li, C. Zhang, Y. Pang, C. Jiang, L. Shao, W. Hu, Z. L. Wang, *Adv. Sci.*
20 **2016**, 3, 1500255.
- 21 [15] K. Dong, J. Deng, Y. Zi, Y. C. Wang, C. Xu, H. Zou, W. Ding, Y. Dai, B. Gu, B. Sun, Z. L.
22 Wang, *Adv. Mater.* **2017**, 29, 1702648.
- 23 [16] Y. M. Lu, W. S. Hwang, W.Y. Liu, J. S. Yang, *Mater. Chem. Phys.* **2001**, 72, 269.
- 24 [17] D. Buc, M. Mikula, D. Music, U. Helmersson, P. Jin, S. Nakao, K. Y. Li, P. W. Shum, Z.
25 Zhou, M. Caplovicova, *J. Electr. Eng.* **2004**, 55, 39.
- 26 [18] J. W. Long, K. E. Swider, C. I. Merzbacher, D. R. Rolison, *Langmuir* **1999**, 15, 780.

- 1 [19] B. Y-L. Chueh, C-H. Hsieh, M-T. Chang, L-J. Chou, C. S. Lao, J. H. Song, J-Y. Gan, Z. L.
2 Wang, *Adv. Mater.* **2007**, *19*, 143.
- 3 [20] S. Bhaskar, P. S. Dobal, S. B. Majumder, R. S. Katiyar, *J. Appl. Phys.* **2001**, *89*, 2987.
- 4 [21] G. J. Exarhos, N. J. Hess, *Thin Solid Films* **1992**, *220*, 254.
- 5 [22] V. Kruefu, A. Wisitsoraat, D. Phokharatkul, A. Tuantranont, S. Phanichphant, *Sensors and*
6 *Actuators B* **2016**, *236*, 466.
- 7 [23] W. Wang, S. Guo, I. Lee, K. Ahmed, J. Zhong, Z. Favors, F. Zaera, M. Ozkan, C. S. Ozkan,
8 *Sci. Rep.* **2014**, *4*, 4452.
- 9 [24] C. Mun, J. J. Ehrhardt, J. Lambert, C. Madic, *Appl. Surf. Sci.* **2007**, *253*, 7613.
- 10 [25] P. K. Nayak, Z. Wang, D. H. Anjum, M. N. Hedhili, H. N. Alshareef, *Appl. Phys. Lett.*
11 **2015**, *106*, 103505.
- 12 [26] S. Narushima, H. Mizoguchi, K. Shimizu, K. Ueda, H. Ohta, M. Hirano, T. Kamiya, H.
13 Hosono, *Adv. Mater.* **2003**, *15*, 1409.
- 14 [27] A. Chasin, M. Nag, A. Bhoolokam, K. Myny, S. Steudel, S. Schols, J. Genoe, G. Gielen, P.
15 Heremans, *IEEE Trans. Electron Devices* **2013**, *60*, 3407.
- 16 [28] Y. C. Shin, J. Song, K. M. Kim, B. J. Choi, S. Choi, H. J. Lee, G. H. Kim, T. Eom, C. S.
17 Hwang, *Appl. Phys. Lett.* **2008**, *92*, 162904.
- 18 [29] Y. Zhang, Z. Mei, S. Cui, H. Liang, Y. Liu, X. Du, *Adv. Electron. Mater.* **2016**, *2*, 1500486.
- 19 [30] M. K. Hota, Q. Jiang, Y. Mashraei, K. N. Salama, H. N. Alshareef, *Advanced Electronic*
20 *Materials* **2017**, *3*, 1700185.
- 21 [31] N. A. Choudhury, A. K. Shukla, S. Sampath, S. Pitchumani, *J. Electrochem. Soc.* **2006**, *153*,
22 A614.
- 23 [32] W. G. Moon, G-P. Kim, M. Lee, H. D. Song, J. Yi, *ACS Appl. Mater. Interfaces* **2015**, *7*,
24 3503.
- 25 [33] K-J. Kim, S-B. Lee, N-W. Han, *Korean J. Chem. Eng.* **1994**, *11*, 41.
- 26 [34] C-C. Liu, D-S. Tsai, D. Susanti, W-C. Yeh, Y-S. Huang, F-J. Liu, *Electrochim. Acta* **2010**,
27 *55*, 5768.
- 28 [35] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, *Nat.*
29 *Commun.* **2014**, *5*, 3754.

- [36] W. Sugimoto, H. Iwata, K. Yokoshima, Y. Murakami, Y. Takasu, *J. Phys. Chem. B* **2005**, 109, 7330.
- [37] P. Huang, C. Lethien, S. Pinaud, K. Brousse, R. Laloo, V. Turq, M. Respaud, A. Demortière, B. Daffos, P. L. Taberna, B. Chaudret, Y. Gogotsi, P. Simon, *Science* **2016**, 351, 691.
- [38] J. Lin, Z. Peng, Y. Liu, F. R. Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, J. M. Tour, *Nat. Commun.* **2014**, 5, 5714.
- [39] Z. S. Wu, K. Parvez, S. Li, S. Yang, Z. Liu, S. Liu, X. Feng, K. Müllen, *Adv. Mater.* **2015**, 27, 4054.
- [40] M. F. El-Kady, R. B. Kaner, *Nat. Commun.* **2013**, 4, 1475
- [41] Z. L. Wang, *Nano Today* **2010**, 5, 512.
- [42] Z. L. Wang, W. Wu, *Angew. Chem.* **2012**, 51, 11700.
- [43] M. A. Karami, D. J. Inman, *Appl. Phys. Lett.* **2012**, 100, 042901.
- [44] M. Beidaghi, Y. Gogotsi, *Energy Environ. Sci.* **2014**, 7, 867.

1

2

3

4 **Figure 1.** (a) Schematic illustration of the integrated microsupercapacitor-thin film rectifier
5 circuits fabricated on a glass substrate; (b) the microsupercapacitor, (c) the field-effect diode
6 rectifier, and (d) a typical single microsupercapacitor/diode unit. In some cases, multiple
7 microsupercapacitors were connected to increase the output potential.

8

Figure 2. (a) Variation of RuO₂ thin film resistivity deposited in different oxygen partial pressures. (b) XRD diffraction patterns obtained from the same RuO₂ films deposited on glass substrate. The inset shows high-resolution XRD spectra for (110) plane. The comparison of (c) Raman and (d) XPS spectra for different RuO₂ thin films. XPS curve fitting revealed the existence of multi oxidation state of Ru and absorbed moisture in the oxide films. (e) The AFM surface profile shows a smooth surface with a surface roughness value of 1.95 nm (R.M.S.). (f) The high-resolution cross-section TEM image of a typical multi-layer stack used to fabricate TFTR.

Figure 3. Optimization of the thin film transistor and rectifier performance with RuO₂ gate contacts. The (a) output, (b) transfer and (c) DC rectification performance obtained from devices using 25 nm ZnO channel thickness. The (d) output, (e) transfer and (f) DC rectification performance obtained from devices using 20 nm ZnO channel thickness. The (g) output, (h) transfer and (i) DC rectification performance obtained from devices using 14 nm ZnO channel thickness. A DC rectification ratio of $\sim 10^7$ was achieved using 14 nm channel thickness. The RuO₂ gate electrode thickness was maintained at 250 nm.

Figure 4. (a) Circuit diagram of the set-up used to measure AC rectification of RuO₂-gated thin film transistor rectifiers. (b) Sinusoidal AC input signals with different amplitudes. (c) Half wave output signals obtained across different external loads. (d) Half wave output signals obtained after the application of different peak to peak voltage-based input signals. (e) Half wave output signals obtained under the application of different input signals carrying different frequency.

Figure 5. Performance of microsupercapacitors sharing same RuO₂ electrodes with thin film rectifiers. (a) CV, (b) CD and (c) effect of glutaraldehyde amount in electrolyte on areal capacitance. (d) CV, (e) CD and (f) effect of RuO₂ electrode thickness on areal capacitance. (g) The CVs and CDs obtained from 250 nm RuO₂ MSCs at different temperatures. (h) Cycling test is showing ~95% capacitance after 10,000 continuous cycles. The inset shows excellent self-discharge characteristics (18.75 mV/hour) can be achieved using our RuO₂ electrodes. (i) CV curve obtained from two identical MSCs connected in series.

Figure 6. Integrated microsupercapacitor-thin film rectifier unit demonstration. Different sinusoidal signals were obtained from a function generator (to simulated harvested energy), stored, and then discharged to power actual device. (a) Charging of MSC using A.C. signals carrying different frequencies. (b) Variation of charging rate at different input frequencies. (c) Charging of MSC using different peak to peak voltage amplitude input signals. (d) Variation of the charging rate at different r.m.s. values of the input signals. (e) Optical image of the actual integrated device, with KAUST logo. (f) Powering off a commercial hygro-thermograph device by the chip shown in (e).

ToC

Integration of Electrochemical Microsupercapacitors with Thin Film

Electronics for On-Chip Energy Storage

Mrinal K. Hota¹, Qiu Jiang¹, Zhenwei Wang¹, Zhong Lin Wang³, Khaled N. Salama^{2}, and*

Husam N. Alshareef^{1,}*

Dr. M. K. Hota, Mr. Q. Jiang, Dr. Z. Wang, and Prof. H. N. Alshareef *

¹Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*E-mail: husam.alshareef@kaust.edu.sa

Prof. K. N. Salama*

²Sensors lab, Advanced Membranes, and Porous Materials Center, Computer, Electrical, and Mathematical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*E-mail: khaled.salama@kaust.edu.sa

Prof. Z. L. Wang

³School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

Keywords: on-chip energy storage, thin film transistor, thin film diode, micro-supercapacitor, RuO₂

On-chip electrochemical energy storage integrated with thin film electronics at the transistor level using a single electrode material (RuO₂) for all devices. The functionality of the integrated devices was successfully demonstrated using alternating signals, which was properly stored, and used to power several electronic devices.

Copyright WILEY-VCH Verlag GmbH & Co. KGaA, 69469 Weinheim, Germany, 2016.

Supporting Information

Integration of Electrochemical Microsupercapacitors with Thin Film

Electronics for On-Chip Energy Storage

Mrinal K. Hota¹, Qiu Jiang¹, Zhenwei Wang¹, Zhong Lin Wang³, Khaled N. Salama^{2}, and*

Husam N. Alshareef^{1,}*

Dr. M. K. Hota, Mr. Q. Jiang, Dr. Z. Wang, and Prof. H. N. Alshareef *

¹Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*E-mail: husam.alshareef@kaust.edu.sa

Prof. K. N. Salama*

²Sensors lab, Advanced Membranes, and Porous Materials Center, Computer, Electrical, and Mathematical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

*E-mail: khaled.salama@kaust.edu.sa

Prof. Z. L. Wang

³School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

Experimental Section

The on-chip MSCs, TFTs, and TFTRs were fabricated on one square inch glass substrates. Device fabrication starts with the cleaning of the glass substrates with acetone, isopropanol, and DI water for 5 min each in an ultrasonication bath. The RuO₂ is deposited at room temperature using a 2-inch Ru target in reactive sputtering mode under argon and oxygen ambient, with 80 W RF power at a deposition pressure of 3 mTorr. Different oxygen partial pressures (O_{pp}), including 0, 8, 16, 20 and 28% O_{pp}, were studied to optimize the deposition

conditions, keeping other parameters constant. For our optimized devices, RuO₂ deposited in 28% O_{pp} was used.

Gel electrolyte: Approximately 2 g of PVA was weighed and transferred onto a 100 ml RB flask containing 20 ml of deionized water to prepare a 10 wt % PVA solution. The mixture was heated at 85 °C with constant stirring until a clear solution of PVA was obtained. This was subsequently cooled to room temperature. Approximately, 2 g of concentrated H₂SO₄ was added to the solution and stirred gently for 30 min to obtain 1:1 PVA-H₂SO₄ solution. Different amounts of glutaraldehyde (GA) was added to get cross-linked gel electrolyte (PVA-H₂SO₄-GA).

Microsupercapacitor devices: The microsupercapacitor (MSC) devices were fabricated using standard microelectronic fabrication and photolithographic processes. The conventional interdigital electrode structure was to fabricate the microsupercapacitors because is compatible thin film transistor fabrication. Each MSC comprised a total of 30 fingers with 100 µm width and 50 µm gap, resulting in an area of 0.0957 cm². Ti (10 nm) and Au (150 nm) bilayer stack was used as the current collector. To get an optimum thickness for the final devices, we studied the RuO₂ thickness effect on MSCs using 125, 250, 500, and 750 nm thick RuO₂ films.

Areal cell capacitance (C_{cell}) was calculated from the charge-discharge curves according to the following equations.

$$\text{Cell capacitance } C_{cell} = \frac{i \cdot \Delta t}{A_{two} \cdot \Delta E} \quad (\text{for 2-electrode configuration}).$$

Where A_{two} is the total area of both the electrodes, ' i ' is the applied current, Δt is the discharge time and ΔE is the potential window.

1 *Field effect devices:* For the field effect devices (TFT and TFTR), atomic layer deposition (ALD)
 2 deposited ~ 130 nm HfO_2 was used as the gate dielectric. Three different thicknesses (14, 20 and
 3 25 nm) of ALD deposited ZnO channel layer was used to optimize the field effect devices. HfO_2
 4 doped ZnO (HZO) conducting oxide film was deposited by ALD was used as the source/drain
 5 material knowing the excellent compatibility with ZnO. The illustration of the device fabrication
 6 process is shown in **Figure S1**.

Figure S1. The schematic illustration of device process flow.

10 *Material and electrical characterization:* The thicknesses of different films were measured by a
 11 surface profilometer (Veeco Decktak 150). Chemical composition and structural analyses of the
 12 films were performed using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD),
 13 and Raman spectroscopy. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer
 14 equipped with a monochromatic $\text{Al K}\alpha$ X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a
 15 multichannel plate, and a delay-line detector under a vacuum of 10^{-9} mbar. The measured
 16 binding energies were corrected with the help of $\text{C } 1s$ (284.8 eV). All XPS spectra were
 17 deconvoluted using the standard Gaussian–Lorentzian function after background correction. In

1 this study, Ru 3*p* core level spectra were analyzed instead of the most intense Ru 3*d*. The peak
2 position for Ru 3*d* spectra coincides with the peak position of C 1*s* spectra, and hence it is hard
3 to distinguish them. A Bruker D8 Discover thin-film X-ray diffractometer and a Horiba Aramis
4 UV spectrometer were used for XRD (Cu K α X-ray source of $\lambda = 0.15406$ nm) and Raman
5 measurements (He-Ne laser of wavelength 633 nm). Electrochemical measurements for the MSC
6 devices used in this study were performed in the two-electrode configuration. The areal and
7 volumetric capacitances of the MSCs were calculated by taking the total area and volume of the
8 electroactive electrodes into consideration. Cyclic voltammetry (CV), galvanostatic charge-
9 discharge (CD), and electrochemical-cycling stability analyses were performed using a VMP3
10 multichannel electrochemical workstation (Bio-Logic). The TFTs and TFTRs DC characteristics
11 were measured using Keysight B1500A semiconductor parameter analyzer. All measurements
12 were carried out at room temperature. Capacitance-voltage was measured by Agilent E4980A
13 precision LCR meter. Agilent 33220A function generator used in high Z mode as the source of
14 the input sinusoidal signals. The input/output signal was monitored in the AC measurements
15 using by Tektronix TDS 2024B oscilloscope.

Figure S2. (a) The variation of RuO₂ resistivity with RF sputter power. The (b) XRD, (c) Raman, (d) XPS spectra obtained from 0% Opp, *i.e.*, pure Ru thin films.

Figure S3. AFM surface morphology obtained from different RuO₂ thin films deposited with Opp of (a) 0%, (b) 8%, (c) 16%, and (d) 20%. The corresponding RMS values of roughness were found as 2.7, 1.17, 1.7, and 1.92 nm respectively.

Figure S4. The schematic of the TFT used in this study

Figure S5. The variation of gate capacitance with applied frequencies. Data measured using RuO₂/HfO₂/RuO₂ stack.

Figure S6. Different output signals obtained using one TFTR with a channel thickness of ~25 nm. No rectification was observed for input frequencies higher than 200 Hz.

Figure S7. Triboelectric nanogenerator (TENG) signal obtained from a homemade TENG device connected to the thin film rectifier, and the output signal obtained from the TFTR connected to the TENG. The TENG input and rectified output signals were measured separately.

Figure S8. Gel electrolyte effect on MSC performance. The CV curves were obtained from (a) 0.5%, (b) 2.5%, (c) 5%, and (d) 10% glutaraldehyde added in the PVA-H₂SO₄ electrolyte. The CD curves were obtained from (e) 0.5%, (f) 2.5%, (g) 5%, and (h) 10% glutaraldehyde added in PVA-H₂SO₄ electrolyte.

Electrochemical impedance spectroscopy (EIS)

The Nyquist plots, measured between 0.1 Hz to 1 MHz, by electrochemical impedance spectroscopy (EIS) show a straight line nearly parallel to the imaginary axis in the low-frequency region, indicating ideal capacitive behavior, as shown in Fig. S9. The characteristic frequency is taken at -45° phase angle where the real and imaginary components have equal magnitude ($Z' = -Z''$). From the high-frequency region in Nyquist plots, the lowest equivalent series resistance (ESR) was found to be $1.9 \Omega \cdot \text{cm}^2$ for the MSCs using 0.5 mass% of GA in the electrolyte. Therefore, PVA-H₂SO₄ gel cross-linked with 0.5 mass% GA was used as electrolyte for the remainder of the study.

Figure S9. EIS spectroscopy data obtained from microsupercapacitors using different amounts of glutaraldehyde in the gel electrolytes.

Figure S10. Effect of active layer (RuO_2) thickness on the CV and CD characteristics of microsupercapacitors. The CV curves were obtained from (a) 125 nm, (b) 250 nm, (c) 500 nm, and (d) 750 nm thick RuO_2 based MSCs. The CD curves were obtained from (e) 125 nm, (f) 250 nm, (g) 500 nm, and (h) 750 nm thick RuO_2 based MSCs.

Figure S11. (a) Volumetric capacitance variation with applied current obtained from MSC with active layer thickness 250 nm. (b) Ragone plot showing energy and power density of the MSC presented in this work along with other reported devices.

Reference:

- [1] C. Zhang, J. Xiao, L. Qian, S. Yuan, S. Wang, P. Lei, *J. Mater. Chem. A*, **2016**, 4, 9502.
- [2] Y. Y. Peng, B. Akuzum, N. Kurra, M. Q. Zhao, M. Alhabeb, B. Anasori, E. C. Kumbur, H. N. Alshareef, M. D. Ger, Y. Gogotsi, *Energy Environ. Sci.*, **2016**, 9, 2847.
- [3] Q. Jiang, N. Kurra, H. N. Alshareef, *Adv. Funct. Mater.*, **2015**, 25, 4976.
- [4] K. Wang, H. Wu, Y. Meng, Z. Wei, *Small*, **2014**, 10, 14–31.
- [5] J. Lin, C. Zhang, Z. Yan, Y. Zhu, Z. Peng, R. H. Hauge, D. Natelson, J. M. Tour, *Nano Lett.*, **2013**, 13, 72–78.
- [6] W. Gao, N. Singh, L. Song, Z. Liu, A. L. M. Reddy, L. Ci, R. Vajtai, Q. Zhang, B. Wei and P. M. Ajayan, *Nat. Nanotechnol.*, **2011**, 6, 496.
- [7] J. Y. Hwang, M. F. El-Kady, Y. Wang, L. Wang, Y. Shao, K. Marsh, J. M. Ko, R. B. Kaner, *Nano Energy*, **2015**, 18, 57.

Figure S12. The experimental circuit diagram of one thin film rectifier-microsupercapacitor unit connected to a function generator (or intermittent energy harvester) and one MSC.

Table S1: Areal and Volumetric Capacitance of Commonly Used Electrode Materials in Electrochemical Capacitors

Electrode material	Electrode thickness (μm)	Electrolyte	Areal Capacitance (mF/cm^2)	Volumetric Capacitance (F/cm^3)	Reference
Carbide-derived carbon	50	1 M H_2SO_4	~450	90	[1]
Mesocarbon	100	Solid-state [BMIM][BF_4]	~100	10	[2]
CDC	4.1	2 M EMI, BF_4 in AN	~84	204	[3]
Graphene	25	1 M H_2SO_4	~16	6.4	[4]
Graphene/PANI	4.5	PVA-based	~326	724	[5]
PEDOT	2.4	1 M H_2SO_4	~36	150	[6]
PPy/C rods	140	0.1 M KCl	~162	12	[7]
Reduced GO	7.6	PVA/ H_2SO_4 polymer gel	~2.3	3	[8]
Reduced GO	0.01	PVA/ H_3PO_4 polymer gel	~0.394	394	[9]
CNT	0.26	0.5 M H_2SO_4	<1	~38	[10]
RuO_2	0.25	PVA/H_2SO_4 polymer gel	3.45	138	This work

References:

- [1] J. Chmiola, C. Largeot, P. L. Taberna, P. Simon, Y. Gogotsi, *Science* **2010**, 328, 480.
- [2] L. M. Miller, C. C. Ho, P. C. Shafer, P. K. Wright, J. W. Evans, R. Ramesh, *Proc. IEEE ECCE* **2009**, 30, 2627.
- [3] P. Huang, C. Lethien, S. Pinaud, K. Brousse, R. Laloo, V. Turq, M. Respaud, A. Demortière, B. Daffos, P. L. Taberna, B. Chaudret, Y. Gogotsi, P. Simon, *Science* **2016**, 351, 691.
- [4] J. Lin, Z. Peng, Y. Liu, F. R. Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, J. M. Tour, *Nat. Commun.* **2014**, 5, 5714.

- 1 [5] Z. S. Wu, K. Parvez, S. Li, S. Yang, Z. Liu, S. Liu, X. Feng, K. Müllen, *Adv. Mater.* **2015**, 27,
2 4054.
- 3 [6] N. Kurra, M. K. Hota, H. N. Alshareef, *Nano Energy* **2015**, 13, 500.
- 4 [7] M. Beidaghi, C. Wang, *Electrochim. Acta* **2011**, 56, 9508.
- 5 [8] M. F. El-Kady, R. B. Kaner, *Nat. Commun.* **2013**, 4, 1475.
- 6 [9] J. J. Yoo, K. Balakrishnan, J. S. Huang, V. Meunier, B. G. Sumpter, A. Srivastava, M.
7 Conway, A. L. M. Reddy, J. Yu, R. Vajtai, P. M. Ajayan, *Nano Lett.* **2011**, 11, 1423.
- 8 [10] T. M. Dinh, K. Armstrong, D. Guay, D. Pech, *J. Mater. Chem. A* **2014**, 2, 7170.
- 9