

Passivation Strategies for Enhancing Solution-Gated Carbon Nanotube Field-Effect Transistor Biosensing Performance and Stability in Ionic Solutions

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Cite This: *ACS Appl. Nano Mater.* 2022, 5, 15865–15874



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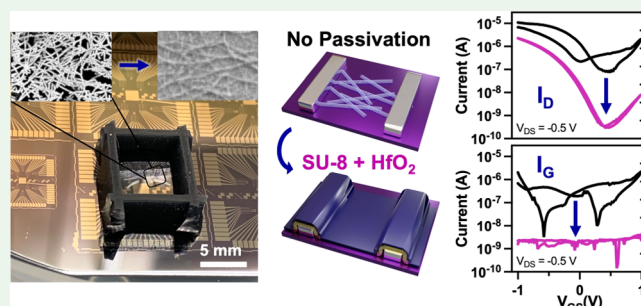
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ABSTRACT: Interest in point-of-care diagnostics has led to increasing demand for the development of nanomaterial-based electronic biosensors such as biosensor field-effect transistors (BioFETs) due to their inherent simplicity, sensitivity, and scalability. The utility of BioFETs, which use electrical transduction to detect biological signals, is directly dependent upon their electrical stability in detection-relevant environments. However, BioFET device structures vary substantially, especially in electrode passivation modalities. Improper passivation of electronic components in ionic solutions can lead to excessive leakage currents and signal drift, thus presenting a hinderance to signal detectability. Here, we harness the sensitivity of nanomaterials to study the effects of various passivation strategies on the performance and stability of a biosensing platform based on aerosol-jet-printed carbon nanotube thin-film transistors. Specifically, nonpassivated devices were compared to devices passivated with photoresist (SU-8), dielectric (HfO_2), or photoresist + dielectric (SU-8 followed by HfO_2) and were evaluated primarily by initial performance metrics, large-scale device yield, and stability throughout long-duration cycling in phosphate buffered saline. We find that all three passivation conditions result in improved device performance compared to nonpassivated devices, with the photoresist + dielectric strategy providing the lowest average leakage current in solution (~ 2 nA). Notably, the photoresist + dielectric strategy also results in the greatest yield of BioFET devices meeting our selected performance criteria on a wafer scale ($\sim 90\%$), the highest long-term stability in solution ($< 0.01\%$ change in on-current), and the best average on/off-current ratio ($\sim 10^4$), hysteresis (~ 32 mV), and subthreshold swing (~ 192 mV/decade). This passivation schema has the potential to pave the path toward a truly high-yield, stable, and robust electrical biosensing platform.

KEYWORDS: BioFET, carbon nanotube field-effect transistor, 1-D nanomaterial, stability, passivation, leakage current, solution gate



1. INTRODUCTION

Increasing demand for personalized medicine and point-of-care diagnostics has led to profound interest in the development of versatile biosensors.¹ Specifically, low-cost, accurate, portable, and robust assessment of biomarkers in physiological solutions (e.g., blood, serum, saliva) is essential for point-of-care biosensing.^{2–5} Common biosensing platforms, such as the enzyme-linked immunosorbent assay (ELISA) and other optical assays, rely on trained personnel and often involve excessively long wait times, making them impractical for personalized use.^{6,7} Compared to optical techniques, electrical detection platforms are inherently simpler, more sensitive, and arguably represent the most practical approach to integrating biosensing into miniaturized and scalable hardware.^{8–11} The proliferation of novel one- and two-dimensional nanomaterials (carbon nanotubes, silicon nanowires, graphene, etc.) has enabled the development of devices with exceptional electrical sensitivities, making these materials highly desirable components in biosensor field-effect transistors (BioFETs).^{12–15}

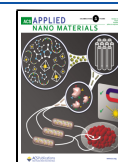
Specifically, semiconducting carbon nanotubes (CNTs) are known for their remarkable sensitivity and mechanical stability, making them an ideal candidate for point-of-care biosensing.^{16,17}

While nanomaterial-based electrical biosensors adhere to many of the tenets of the so-called “ideal biosensor,” one fundamental issue that could limit their success is unwanted leakage current, often referred to as gate leakage (I_G).¹⁸ Upon immersion in ionic solutions, improper passivation of the transistor components, such as the conductive source/drain electrodes and the semiconducting channel, results in the

Received: September 16, 2022

Accepted: September 20, 2022

Published: October 4, 2022



diversion of electrical current (i.e., the signal) from the desired source–channel–drain path to a leakage path that travels through the ionic solution. Thus, a detectable signal shift may be caused by sensor drift due to gate leakage, which hinders biodetection by making it difficult to attribute changes in a transistor's electrical performance characteristics directly to biomolecular interactions with the semiconducting channel.¹⁹ These leakage effects would result in observable changes in key transistor performance metrics like on/off-current ratio, hysteresis, and subthreshold swing (SS), thus dampening the detectable biomarker signal.

Unfortunately, the discussion of leakage currents is one that has been underreported in the BioFET space. While the issue of parasitic currents in transistors operating in air (or non-liquid-gated devices) is well documented, with several examples of passivation-focused studies aimed at minimizing these artifact currents,^{20–26} the same discussion of gate leakage mitigation strategies is one that has been missing from the solution-gated transistor space. Several reports have discussed the importance of leakage current reduction in these devices,^{19,27,28} as well as called for the reporting of leakage currents in relevant applications, but a consistent and reliable encapsulation strategy to overcome the issue remains unclear. While a large number of studies ignore it altogether, some address the challenge of leakage current from BioFETs by simply mentioning the incorporation of an insulator like SU-8,^{29,30} silicone rubber,³¹ or polyimide³² in their device structure. However, justification behind the choice of insulator is seldom provided or compared to other possible candidates. Similarly, the placement of the insulator is often varied between covering just the metal contacts or the entire device (contacts + channel), and this variation in strategy—both in material choice and placement—would undoubtedly influence performance and stability in the resulting BioFETs. Therefore, determining initial transistor performance and long-term stability for various passivation strategies is of paramount importance to ion-sensitive field-effect transistors, especially those used in biological applications. So far, significant focus in the field has been on developing novel applications, yet there is no consensus on device design, which leads to difficulty comparing results between reports that ostensibly investigate similar phenomena. Thus, it remains imperative that a systematic means of addressing leakage current and passivation in liquid-gated devices be determined.

In this work, we investigate various passivation strategies for printed, solution-gated CNT BioFET platforms. Contact-only photoresist passivation is investigated alongside whole-device dielectric passivation, predominantly in the context of leakage current reduction, device stability throughout testing, and wafer-scale device yield. We find that while optimized photoresist-only and dielectric-only passivation both result in high-quality BioFETs, the combination of the two—contact passivation with photoresist and entire device passivation with a dielectric—results in the lowest average leakage current (~ 2 nA), as well as highly consistent performance, with nearly 90% of tested devices simultaneously displaying nA-level gate leakage, on/off-current ratios $> 10^3$, hysteresis < 75 mV, and SS < 300 mV/decade in solution. The photoresist + dielectric strategy also results in the best stability over 400 testing cycles, demonstrating robust performance on a timescale exceeding that required for most biomolecular binding interactions. Finally, we show that the addition of a poly(ethylene glycol) (PEG) polymer layer, which reduces nonspecific protein

adsorption and increases Debye length, has no adverse impact on device performance and does not interfere with long-term cycling when polymerized on our passivation structures.

2. EXPERIMENTAL SECTION

2.1. Contact Deposition. All devices were fabricated on a 4-in p-doped Si wafer with a thermally grown $2\ \mu\text{m}$ SiO_2 oxide (University Wafer). The Si wafer was first cleaned by sonication in acetone, followed by isopropyl alcohol, and then water. Immediately before processing, oxygen plasma was performed to eliminate any remaining organic and inorganic contaminants. Next, the wafer was coated with P20 primer and S1813 photoresist using a spin-coater (500 rpm for 5 s, 3000 rpm for 30 s for each) and then baked at $115\ ^\circ\text{C}$ for 60 s. The wafer was then patterned with a $365\ \text{nm}$ UV light for 11 s using a Karl Suss MA6/BA6 photomask aligner at $120\ \text{mJ}/\text{cm}^2$. The exposed wafer was subsequently developed in MF319 developer for 60 s, rinsed with deionized water, and then gently blown dry with N_2 gas. Next, 5 nm of Cr and 30 nm of Pd were deposited using a CHA Industries Solution E-Beam Evaporator, coating the wafer with Cr/Pd. Finally, the wafer was sonicated in acetone for 15 min to selectively lift-off or remove the metal from the nonpatterned regions.

2.2. Carbon Nanotube Aerosol Jet Printing. After metal contact deposition, transistor channels were created by aerosol jet printing carbon nanotube films between metallic components, creating source, drain, and channel regions. Prior to CNT printing, the substrates were functionalized by immersion in poly-L-lysine solution (0.1% w/v in water, Sigma-Aldrich) for 5 min, followed by a thorough DI water rinse and gentle blow drying using N_2 . High-purity ($>99.9\%$) single-walled semiconducting carbon nanotube ink (IsoSol-S100, Nanointegris Inc.) was diluted to a concentration of $0.005\ \text{mg}/\text{mL}$ using toluene (Sigma-Aldrich). Terpineol ($10\ \mu\text{L}/\text{mL}$, Sigma-Aldrich) was added to the ink to increase the viscosity of the solution for higher print quality. Two milliliters of the resulting ink was loaded into the ultrasonic atomizer of the aerosol jet printer (Optomec 300 Series Aerosol Jet Printer), and CNTs were printed at room temperature using a $150\ \mu\text{m}$ nozzle, 30 sccm sheath flow rate, 20 sccm carrier gas flow rate, 410 mA ultrasonic current, and a printing speed of $8\ \text{mm}/\text{s}$ with two print passes. The wafers were then removed from the printer and placed in an oven at $200\ ^\circ\text{C}$ for 3 min to evaporate the remainder of the solvent. Next, a rapid thermal annealing (RTA) system (Jipelec JetFirst 100) was used to anneal the CNT channels and drive off excess polymer residue.³³ The RTA process was run under vacuum (~ 1 Torr) at $500\ ^\circ\text{C}$ for 8 min with a 2-min temperature ramp. Finally, the wafer was diced into chips using a dicing saw (Disco DAD3220).

2.3. SU-8 Photoresist Passivation. SU-8 TF 6000.5 photoresist (Microchem) was spun onto the substrates using a spin-coater (500 rpm for 5 s, 3000 rpm for 30 s). Next, the substrates were exposed to UV light (various soft-bake conditions, $120\ \text{mJ}/\text{cm}^2$ exposure for 9 s) and baked on a hot-plate post-exposure for 1 min. Finally, the substrates were developed in SU-8 developer (Microchem), rinsed with isopropyl alcohol followed by DI water, and gently blown dry with N_2 .

2.4. Atomic Layer Deposition of HfO_2 . A hafnium dioxide (HfO_2) dielectric layer was deposited using an atomic layer deposition (ALD) system (Kurt J. Lesker 150LX) at $120\ ^\circ\text{C}$ and 1 Torr. Tetrakis(dimethylamido)hafnium(IV) heated to $85\ ^\circ\text{C}$ was used as the Hf precursor (pulse time of 10 ms), with water vapor acting as the oxygen precursor (pulse time of 30 ms). The purge time for both precursors was 10 s, and they were run for 250 cycles to yield $\sim 30\ \text{nm}$ of HfO_2 . For the thinner dielectric studies presented in Figure S5, a 2 nm Al seed layer was deposited on the wafer using an electron-beam evaporator (at a rate of $0.5\ \text{\AA}/\text{s}$) prior to ALD, which was run for 67 cycles to yield $\sim 8\ \text{nm}$ of HfO_2 .

2.5. Poly(ethylene glycol) Immobilization. Poly(ethylene glycol) was immobilized onto the carbon nanotube thin-film transistor (CNT-TFT) surface using a covalent coupling technique demonstrated by Sharma et al.³⁴ In short, 4 g of $1000\ \text{M}_n$ PEG was sonicated in 100 mL of anhydrous toluene until fully dissolved. Triethylamine

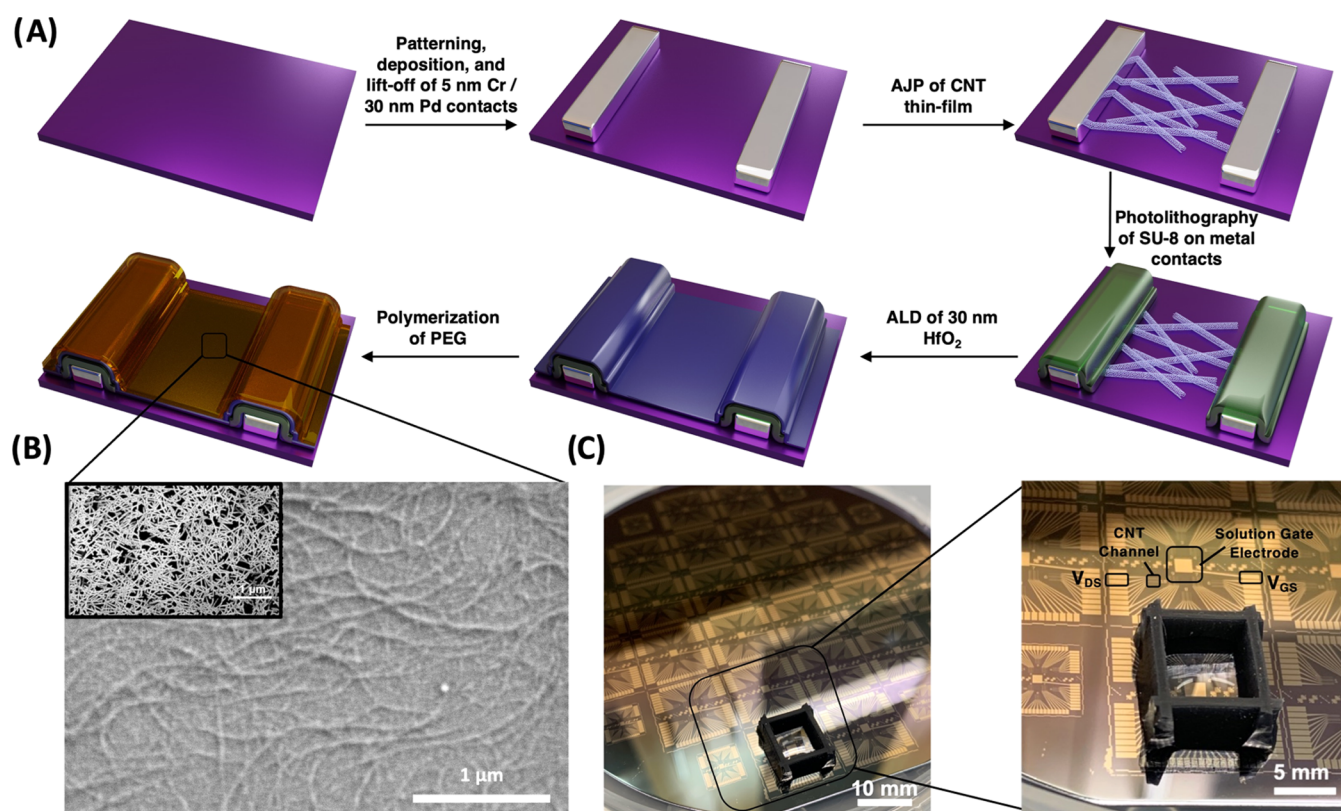


Figure 1. Fabrication process and device layout for solution-gated CNT BioFETs in this work. (A) Schematic outline of fabrication and passivation processes. (B) SEM image of a carbon nanotube thin film encapsulated by HfO₂ and PEG in the channel region, with an inset showing the aerosol jet-printed CNT channel without HfO₂ or PEG. (C) Image of a chip immersed in PBS (the solution gate) contained by a rubber gasket with the inset image highlighting electrode locations for a neighboring chip. Note, leakage current (I_G) is measured at the solution gate where V_{GS} is applied.

(544 μL) was added dropwise to the dissolved PEG solution and stirred slowly for 1 h. Then, 57.14 μL of silicon tetrachloride was added dropwise to the solution and stirred slowly for 15 more min. The solution was then filtered through a sintered glass funnel, and CNT-TFT chips were placed in the solution for 30 min. After completion, the chips were removed, rinsed with DI water, and gently blown dry with N₂. In this process, PEG is covalently coupled to the free hydroxyl groups present on the SiO₂ substrate around and within the CNT thin film (owing to the presence of gaps within the film as seen in the inset of Figure 1B) for nonpassivated and SU-8-passivated devices, and those readily available on HfO₂ surfaces for devices with dielectric passivation (HfO₂ and SU-8 + HfO₂ encapsulated devices). PEG, triethylamine, silicon tetrachloride, and anhydrous toluene were all purchased from Sigma-Aldrich.

2.6. Device Characterization. Scanning electron microscopy (SEM) of the CNT channel was performed using an Apreo 2 SEM by ThermoFisher Scientific, with an accelerating voltage of 2.00 kV and an emission current of 25 pA at 35 000 $\times$ magnification (25 000 $\times$ for cross-sectional imaging of SU-8). X-ray photoelectron spectroscopy (XPS) characterization was performed using an AXIS Ultra Photoelectron Spectrometer (Kratos Analytical) operating at 15 kV and 10 mA. Optical microscopy images of the devices were obtained using a Zeiss Axio Lab compound microscope at 5 $\times$ magnification. Profilometry of SU-8 and metal contacts was done using a Bruker Dektak 150 profilometer at a resolution of 0.078 $\mu\text{m}/\text{sample}$. Finally, all electrical testing was done by physically pressing down a rubber gasket onto the CNT-TFT chips, adding 100 μL of 1 $\times$ phosphate buffered saline (PBS) (Corning), and testing under ambient conditions using a Signatone H150W tabletop probe station connected to an Agilent B-1500 semiconductor parameter analyzer. All transfer curves were tested at a V_{GS} of -1 to $+1$ V and a V_{DS} of -0.5 V.

3. RESULTS AND DISCUSSION

The process flow diagram of the fabricated CNT-TFTs is shown in Figure 1A. An Optomec AJ300 aerosol jet printer was used to print the carbon nanotube channels (channel length $L_{ch} = 50$ μm , channel width $W_{ch} = 175$ μm) over lithographically defined Pd source and drain contacts. Aerosol jet printing (AJP) is a direct-write fabrication method that enables rapid prototyping with high degrees of customizability while offering highly stable and uniform devices.^{33,35–38} Scanning electron microscopy verified the uniformity of these channels by showing a percolated CNT network (Figure 1B) with a film morphology consistent with those shown to yield high-performance transport characteristics in the literature.^{39–41} After transistor fabrication, the devices were separated into different categories depending on their passivation conditions: (1) no passivation, (2) photoresist-only passivation, (3) dielectric-only passivation, and (4) photoresist + dielectric passivation. Photoresist passivation of the contacts was done using SU-8 6000.5, a ~ 400 nm thick epoxy-based negative photoresist using a pattern that covers all source/drain contacts but leaves the solution-gate electrode and channels exposed. Notably, SU-8 is exceptionally stable, patternable, biocompatible, and provides insulating properties required for the mitigation of direct electrical access of the ionic solution to the metal contacts.^{29,42–45} Next, the devices were passivated with a HfO₂ dielectric using ALD on chips with and without SU-8, yielding photoresist + dielectric and dielectric-only passivated devices, respectively. ALD is a sequential and self-limiting chemical deposition technique that allows for thickness control on the nanometer scale and

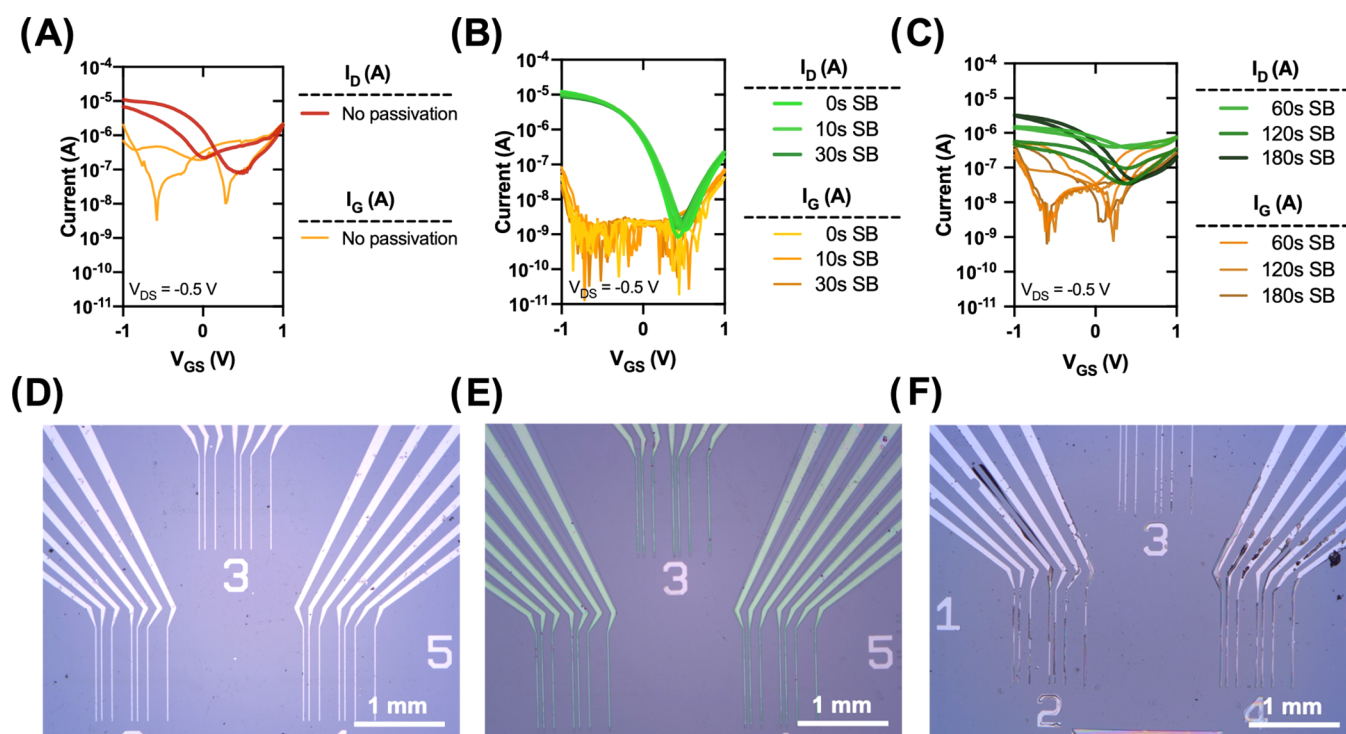


Figure 2. SU-8 passivation and the role of soft-bake time. Transistor subthreshold curves and microscopy images under various SU-8 conditions for solution-gated devices. (A, D) No SU-8 passivation; (B, E) SU-8 passivation fabricated with 0, 10, and 30 s soft-bake (SB); and (C, F) SU-8 passivation fabricated with 60, 120, and 180 s soft-bake, showing evidence of residual photoresist and metal contact delamination.

offers exceptional uniformity with markedly low defect densities, enabling the use of ALD-grown dielectrics in modern transistors.^{46–49} Thus, ALD was used to encapsulate the entire device with an insulating high- κ dielectric. We chose HfO_2 as the insulator of choice due to its high dielectric constant (~ 25) compared to SiO_2 (3.9), Al_2O_3 (9), and Si_3N_4 (7), leading to improved gate capacitance effects for amplified BioFET sensitivity.⁵⁰ Finally, chips were coated in poly(ethylene glycol) to assess device performance with the presence of an antifouling biofunctional layer. All fabricated devices were tested in a solution-gated environment by pressing down a rubber gasket and immersing the source, drain, and channel regions of the device in 1× PBS, while keeping the probes and contact pads dry (Figure 1C). The gate signal was applied to the 1× PBS solution using the on-chip Pd solution-gate electrode, as shown by the metallic square in the center of the chip in Figure 1C.

Defect-free fabrication of SU-8 on the metal source/drain contacts is essential for the mitigation of leakage current. A major issue that arose throughout the SU-8 passivation process was significant chip-to-chip variation in SU-8 film quality when following manufacturer instructions, ranging from partial to complete delamination. Given the multistep fabrication process for SU-8 films, we wanted to understand which process step was responsible for the variability. We investigated the photoresist fabrication process by studying the effects of soft-bake (pre-exposure) time, exposure time, and post-bake time, both with and without an adhesion promotion layer. As shown in Figure 2, the main source of inconsistency in SU-8 film quality was the soft-bake time. Devices tested with soft-bake times of 60 s and above (Figure 2C) showed similar performance to those with no passivation at all (Figure 2A), exhibiting high variability, poor switching behavior (on/off-current ratios $<10^2$), high hysteresis (>75 mV), and

appreciably high levels of leakage current (up to μA level). Conversely, SU-8 devices fabricated with lower soft-bake times of 0–30 s (Figure 2B) exhibited consistent performance, with drastic improvements in switching behavior, hysteresis, and leakage. These effects are further elucidated in Figure S1, which shows that leakage current is low and on/off-current ratios are high for devices fabricated with soft-bake times of 0–30 s and vice versa for devices made with soft-bake times of 60 s and above. Optical microscopy imaging of the Pd contacts without passivation (Figures 2D and S2A) and following a 60 s soft-baked SU-8 step (Figures 2F and S2C) indicates visual concordance, with both showing a silver-like color that is characteristic of bare Pd. The 60 s soft-baked SU-8 also shows remnants of photoresist, evidential of significant delamination. Contrarily, imaging of Pd contacts with 0–30 s soft-baked SU-8 (Figures 2E and S2B) shows a pristine SU-8 film, as indicated by a uniform green hue on the contacts that is characteristic of SU-8. A cross-sectional SEM image of this pristine SU-8 film is presented in Figure S2D, showing a ~ 1 μm extension beyond the contact, which is a parameter that could play a role in the quality of SU-8's ability to passivate the electrodes.⁵¹ The effects of soft-bake times are further confirmed by profilometry studies, which show that non-passivated contacts (Figure S3A) and intact SU-8-passivated contacts made with a <30 s soft-bake (Figure S3B) consistently yield heights of ~ 40 and ~ 450 nm, respectively, whereas delaminated SU-8 (resulting from soft-bake times >60 s) yields unpredictable and nonuniform heights (Figure S3C). The average values collected over several measurements in Figure S3D for each contact also contrast the consistency in the height profile of intact SU-8 and the high variability of delaminated (>60 s soft-baked) SU-8. Altogether, these results provide evidence of the deleterious effects of internal thermal stresses in SU-8 caused by prolonged soft-bake times of 60 s

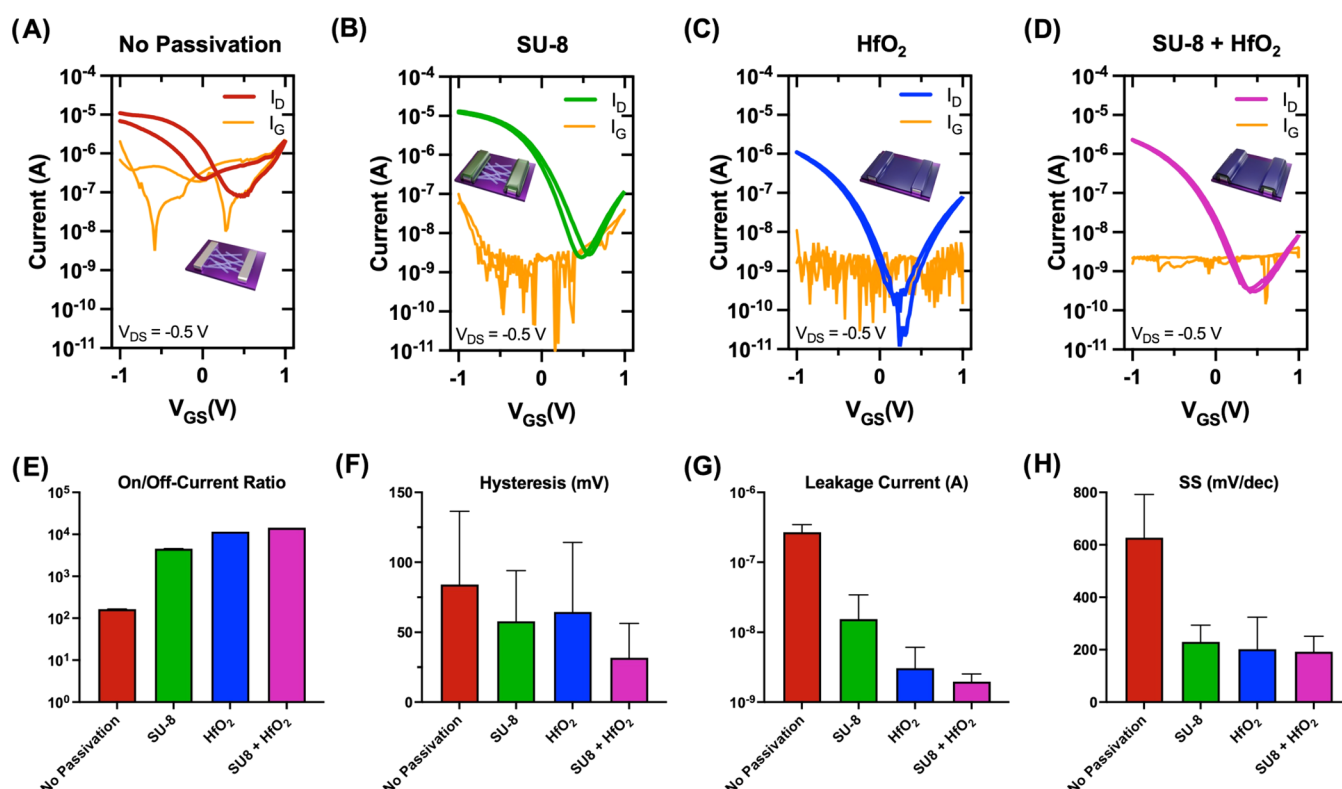


Figure 3. Impact of passivation strategy on key performance metrics. Typical transistor subthreshold curves for various passivation conditions and relevant performance metric averages for each passivation condition. Subthreshold curves for a solution-gated device with (A) no passivation, (B) SU-8 only passivation, (C) HfO_2 only passivation, and (D) SU-8 + HfO_2 passivation. Plots comparing averages with one standard deviation of key performance metrics, including (E) on/off-current ratio, (F) hysteresis (measured ~ 1 order of magnitude above the minimum current for each condition), (G) leakage current, and (H) subthreshold swing.

and above, similar to those shown by others in the literature.^{44,52} Consequently, all photoresist-passivated devices in this study were fabricated using SU-8 with a soft-bake step between 0 and 30 s.

After optimizing the SU-8 passivation layer fabrication procedure, the electrical performance of the BioFET devices under various passivation conditions could be compared. The purpose of this investigation was to determine the optimal passivation schema of transistors in ionic solutions to yield a robust transistor-based platform for successful biodetection. To achieve this, low gate leakage currents (and by extension, high on/off-current ratios) as well as minimal hysteresis are desired.^{19,53} It was observed that devices without any passivation layers performed inadequately in solution-gated environments, displaying significant device-to-device variation, poor switching behavior (on/off-current ratio $< 10^2$), high hysteresis, and most significantly, leakage currents between 100 nA and 1 μ A (Figure 3A). Since analytes are typically small in size and charge, the minimization of leakage currents is necessary to prevent those charges from being obscured in the solution, rendering them undetectable by a BioFET. Conversely, devices passivated with SU-8 (Figure 3B), HfO_2 (Figure 3C), and SU-8 followed by HfO_2 (Figure 3D) showed substantial improvements in all parameters, as illustrated by their subthreshold curves. Figure S4 presents these subthreshold curves separated into drain current (Figure S4A) and gate leakage current (Figure S4B) plots to aid in visualizing the current effects of each passivation layer. The average on/off-current ratio (Figure 3E), hysteresis (Figure 3F), leakage current (Figure 3G), and subthreshold swing (Figure 3H) for

each passivation condition further elucidates the improvements offered by each passivation strategy. These metrics were extracted and averaged from 20 nonpassivated devices, 78 SU-8-passivated devices, 23 HfO_2 -passivated devices, and 63 SU-8 + HfO_2 passivated devices. The devices tested for each passivation strategy came from several different chips (with each chip containing ~ 4 tested devices) to capture device-to-device and chip-to-chip variability simultaneously.

As metal contacts become completely encapsulated by a thick insulating photoresist like SU-8, the metal and the ionic solution become electrically isolated from one another, reducing the magnitude of leakage current. This substantiates a commonly observed phenomenon whereby any type of insulation between the electrodes and the ionic solution provides great benefit to device performance due to some degree of carrier blocking between the metal and the surrounding solution. When the entire device is instead encapsulated by a 30 nm HfO_2 dielectric, a similar effect is observed, though the HfO_2 provides stronger carrier transport blocking from the solution than SU-8 alone. This improvement is attributed to a combined effect of reduced pinhole defect density within the material (as ALD-grown materials have lower defect densities than spin-coated photoresists owing to the controlled layer-by-layer growth mechanism) and the ability to passivate the CNT thin-film channel from its surrounding environment, thus limiting exposure to traps that may affect carrier transport.²⁵ Even though the insulating dielectric is covering the CNT channel and increasing the distance between any potential surface-deposited biomolecules and the channel itself, it is thin enough to allow for chemical

Table 1. Wafer-Scale Comparison of Selected Performance Metrics for Devices with Different Passivation Conditions

	no. of devices	$I_G < 10$ nA	hysteresis < 75 mV	SS < 300 mV/dec	on/off $> 10^3$	devices meeting all performance criteria
no passivation	20	0 (0%)	6 (30%)	3 (15%)	3 (15%)	0 (0%)
SU-8	78	49 (63%)	51 (65%)	67 (86%)	76 (97%)	36 (46%)
HfO ₂	23	22 (96%)	14 (61%)	20 (87%)	20 (87%)	12 (52%)
SU-8 + HfO ₂	63	60 (95%)	61 (97%)	58 (92%)	61 (97%)	56 (89%)

gate-coupling effects. Moreover, this passivation layer results in the removal of competing biosensing mechanisms (e.g., by suppressing Schottky barrier effects resulting from biomolecular reactions near the contacts, and instead causing electrostatic gating at the channel to dominate the sensing signal), as well as the reduction of artifact currents (e.g., leakage) and signal noise, which decrease sensitivity to biomarker signals.^{54,55} Reports have shown that HfO₂ thicknesses of 25, 30, and 50 nm in similar nanomaterial-based BioFETs have resulted in detection limits of 100 nM, 60 fM, and 225 nM, respectively, making 30 nm a viable target dielectric thickness for the majority of devices in this work.^{56–58} Finally, the enhanced stability and patternability (e.g., by creating a uniform surface chemistry that enables the polymerization of Debye length modulating polymers⁶¹) that result from having the dielectric interlayer make it a valuable addition.

To further investigate the effects of using a thinner dielectric layer, a set of 23 devices were fabricated using 8 nm of HfO₂ deposited on a 2 nm Al seed layer (Figure S5), which is typically regarded as a minimum dielectric thickness on unfunctionalized CNTs due to the difficulty in ALD nucleation owing to their inherent chemical inertness.^{59,60} From this investigation, it was evident that the use of an 8 nm dielectric (even when paired with SU-8 on the contacts) led to significant device-to-device variation, where a few devices showed subthreshold curves consistent with the expected ambipolar behavior seen with other passivation conditions (Figure S5A), but the majority showed behavior that was either completely nonfunctional, or dominated by gate leakage current I_G (Figure S5B). Although the measured average leakage current was still an improvement compared to SU-8 alone, it was notably higher than the 30 nm dielectric (Figure S5C). Additionally, the low device yield and performance when compared to the 30 nm dielectric (Figure S5D) presents perhaps the most significant issue with using a thinner dielectric, as it would prevent reliable measurements for that passivation strategy. As a result, a 30 nm HfO₂ thickness was targeted in all remaining studies to minimize leakage currents while preserving sensitivity and maximizing yield.^{56–58}

The photoresist + dielectric combination provides the best improvement in on/off-current ratio, leakage current, hysteresis, and SS. The advantageous performance of the dual-layer encapsulation is attributed to the high resistance to leakage current of a thick insulator on the metal contacts and the signal transducing transparency of a thin high- κ dielectric covering the entire device to further reduce leakage current while also minimizing interface trap effects. Another added insight provided by the data shown in these experiments is of the effects of encapsulation on factors like hysteresis, on/off-current ratio, and subthreshold swing, all of which are significantly affected by the presence (and subsequent reduction of) leakage currents. Additionally, while using a photoresist-only strategy may not be the most preferable in terms of performance metrics compared to the other two strategies, it does still show a drastic improvement compared

to nonpassivated devices. While not ideal, it could nevertheless work well at improving performance in situations where ALD fabrication methods are incompatible or if the channel must be directly accessible to the surrounding environment.

Given that nanomaterial-based transistors are known for their high device-to-device variability,⁶² determining the wafer-scale device yield in the context of key electrical performance metrics is critical. A large-scale study was performed, as shown in Table 1, where yield and percentage for each passivation condition is evaluated based on the number of devices meeting certain performance metric thresholds (leakage current (I_G) < 10 nA; hysteresis < 75 mV; SS < 300 mV/decade; and on/off-current ratio $> 10^3$) compared to the total number of tested devices (as previously mentioned, ~ 4 devices were tested per chip). Additionally, the table presents the yield of “Devices Meeting All Performance Criteria” from the wafer-scale batch of chips, which are devices that meet all four performance metrics thresholds simultaneously. We postulate that given our specific device setup, a robust, sensitive, and well-performing electrical biosensor is one that meets these leakage current, hysteresis, SS, and on/off-current ratio criteria. Selection of the particular thresholds for these performance metrics was based on maximizing overall BioFET utility in sensing applications where it is important to minimize noise while achieving sufficiently high signal response at low voltages. Notably, this table indicates that the yield does roughly correlate with the statistical data shown in Figure 3E–H, with SU-8-only passivation offering a substantial improvement to nonpassivated devices in all four metrics, resulting in an increase from 0 to 46% in the yield of transistors that meet our requirements for a biosensor. HfO₂-passivated devices (with or without SU-8 underneath) were the most effective at reducing gate leakage; however, HfO₂-only devices did not perform as well as SU-8-only in hysteresis and on/off-current ratio. Nevertheless, HfO₂ devices did result in an improvement in biosensor-compatible yield compared to SU-8, with 52% of tested devices falling in the high-performance category. Finally, the addition of HfO₂ onto SU-8 offered the highest yield in low hysteresis (97%), low SS (92%), and high on/off-current ratio (97%) devices, as well as similarly high yield in low gate leakage (95%), resulting in an impressive 89% yield of devices that meet all desired performance criteria. Ultimately, these results show that the presence of both SU-8 and HfO₂ is necessary for the highest possible yield of biosensor-compatible devices based on our performance criteria.

Since biosensors require some incubation time for binding events and reactions to occur, it is imperative that BioFETs maintain stability in their electrical performance throughout the entirety of a given testing period in solution. Though these testing durations are relatively short (typically on the order of minutes), we sought to investigate the stability of representative devices under various passivation conditions for 400 testing cycles spanning 2 h. By examining stability in a relatively large testing window, we can understand how these passivation structures compare at combating instabilities that

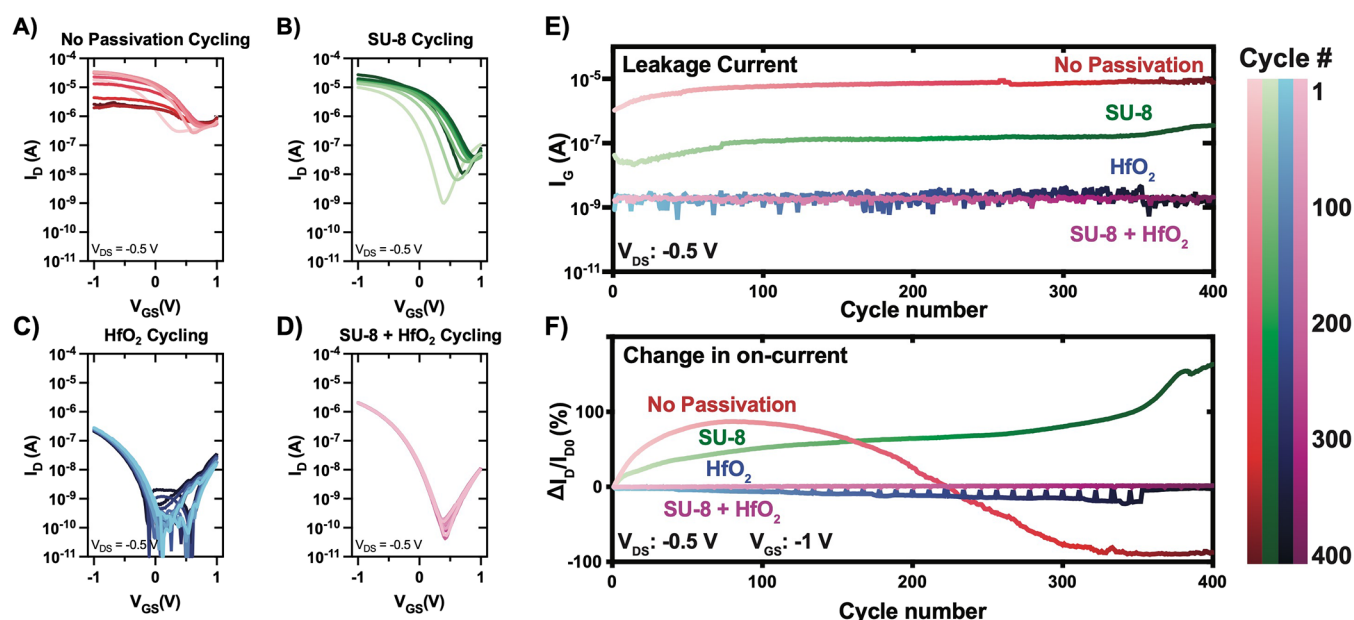


Figure 4. Impact of long-term voltage cycling on BioFET stability. Subthreshold curves of solution-gated devices cycled over 2 h (400 cycles) with (A) no passivation, (B) SU-8-only passivation, (C) HfO₂-only passivation, and (D) SU-8 + HfO₂ passivation. (E) Leakage current for all passivation conditions. (F) Percent change in on-current at a V_{GS} of -1 V.

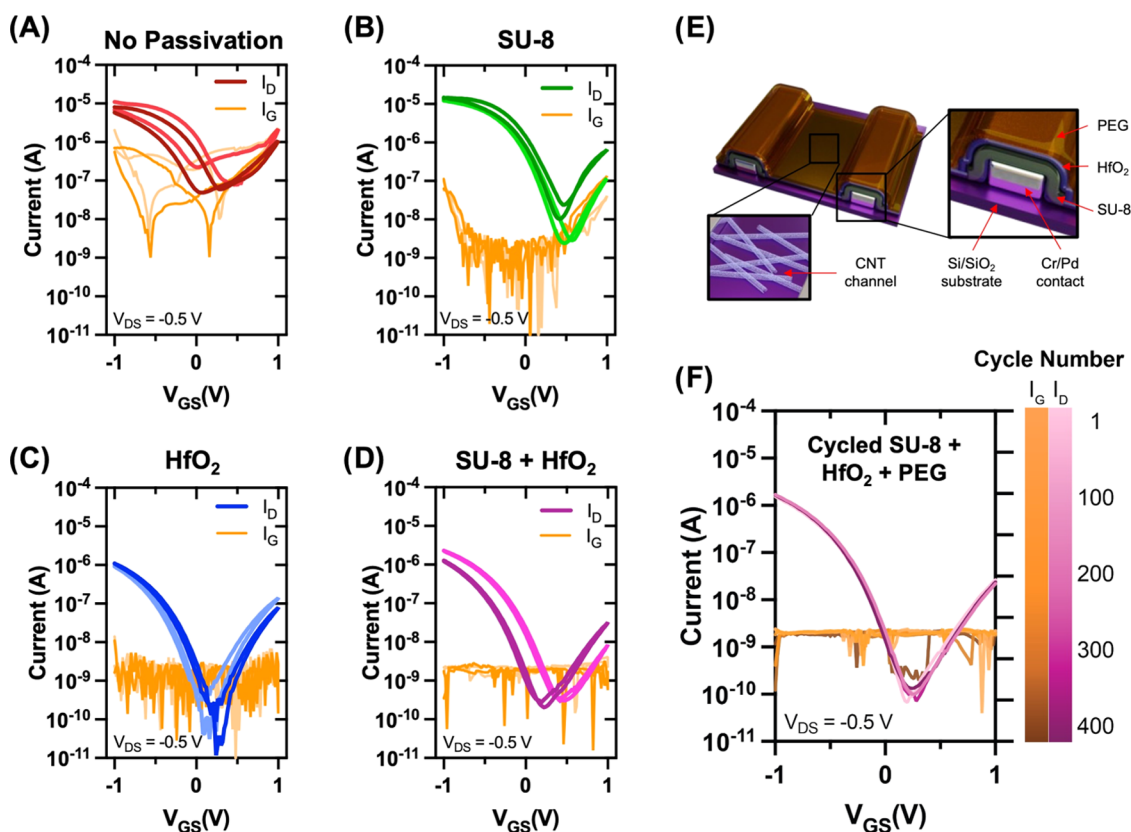


Figure 5. Electrical characterization of solution-gated devices after the addition of a final PEG polymer layer. (A–D) Subthreshold curves before (lighter color) and after (darker color) PEG polymerization. (E) Schematic of CNT BioFET after the addition of PEG. (F) Long-term cycling (400 cycles over 2 h) of an SU-8 + HfO₂ passivated device after PEG polymerization.

present in the form of signal drift and leakage current throughout extended testing durations. After nonpassivated devices (Figure 4A), the SU-8-only passivated devices (Figure 4B) showed the poorest retention of quality over 400 testing cycles (2 h), as there was an increase in the leakage current

over time (Figure 4E) and a gradual drift in the subthreshold curve, both by roughly one order of magnitude. HfO₂-only devices (Figure 4C) showed considerable enhancement in stability, although drift and noise were still prevalent. Rather impressively, the SU-8 + HfO₂ encapsulated devices (Figure

4D) showed extremely stable performance, with no considerable change in either leakage or the subthreshold curve (and subsequently, transistor metrics) over 400 cycles. This result is highly promising for the future of solution-gated biosensing as it demonstrates the ability to maintain stable and accurate device metrics over time. To further illustrate the stability of these devices, Figure 4F depicts the normalized change in on-current—a metric frequently used in electrical biosensor applications—as a function of the cycle number. Similar to previous results, the nonpassivated and SU-8-only passivated devices yielded the highest drift over time, rendering them incompatible for use in long-term sensing applications. HfO_2 -passivated devices showed a minor decrease in on-current stability over time, resulting in a 0.03% change in on-current after 400 cycles, and a maximum of 0.23% change. Remarkably, SU-8 + HfO_2 passivated showed marked stability over time, resulting in only a 0.016% change in on-current after 400 cycles and a maximum of 0.016% change throughout those 400 cycles, proving its suitability as a robust and stable biosensing platform.

Having demonstrated the initial performance, yield, and long-term stability of devices with these encapsulation materials, we then sought to determine device compatibility with a biofunctional layer. PEG is a hydrophilic polymer, well known for its ability to prevent adventitious adsorption of biomolecules, as well as its ability to extend the Debye length in ionic solutions.^{61,63,64} In Figure S6, we verified the growth of PEG by comparing XPS signatures of a sample high- κ dielectric (Al_2O_3) surface before (dotted line) and after (solid line) polymerization. The XPS analysis shows a significant increase in the C and Si moieties on the surface (as SiCl_4 was used as a reactant), matching the expected PEG signature. Additionally, the drastic decrease in Al concentration after polymerization verifies the successful tethering of PEG on the surface, as XPS only has a penetration depth of up to ~ 10 nm for Al $K\alpha$ radiation.⁴ The water contact angles shown in the inset of Figure S6 demonstrate a major increase in the hydrophilicity of the surface after polymerization, as expected from a hydrophilic polymer like PEG. To determine how well devices could maintain their electrical characteristics after the addition of PEG, we retested the same devices shown in Figure 3A–D (light colored curves) post-polymerization (Figure 5A–D). Markedly, nonpassivated devices showed a shift in both I_G and I_D curves, whereas all passivated devices showed small shifts in the I_D curves (as is expected after the addition of a charged polymer species) but nearly negligible shifts in I_G , verifying the ability for these encapsulation layers to maintain the sought-after low leakage current properties. Finally, the best passivation condition (SU-8 + HfO_2) was tested after the addition of PEG (as shown by the schematic in Figure 5E) for 400 cycles (Figure 5F), maintaining high levels of stability over 2 h and showing concordance with Figure 4D even after the addition of PEG. Ultimately, this verifies that this passivation condition is stable and sensitive enough to yield a measurable shift in the threshold voltage with the occurrence of molecular interactions even in the presence of encapsulation layers.

4. CONCLUSIONS

In conclusion, a method of tackling the issue of leakage current in solution-gated nanomaterial-based BioFETs is presented using a carbon nanotube thin-film transistor, providing insight into the role of passivation strategies in the development of a robust electrical biosensing platform. Metal contact-only

passivation using ~ 400 nm thick SU-8 layers of various soft-bake times was shown compared with whole-device passivation using 30 nm of a high- κ dielectric (HfO_2), both with and without SU-8 over the contacts. Ultimately, it was discovered that the devices with the greatest general improvement in target metrics (leakage current, on/off-current ratio, hysteresis, and subthreshold swing), biosensor-compatible device yield, and long-term stability were devices fabricated with <60 s soft-baked SU-8 on the contacts and then full encapsulation by a 30 nm HfO_2 layer. Notably, photoresist + dielectric-passivated devices performed the best at reducing the leakage current, as well as providing the highest overall device yield based on target performance metrics. Furthermore, the ability to maintain these stable results with the addition of PEG demonstrates the compatibility of this BioFET platform with various biosensing applications. These results provide critical insight on the considerable performance improvements and implications stemming from optimized passivation layers, and in particular, the implementation of a dual-passivation strategy (encapsulation of both the metal contacts and the channel), which is much less commonly observed in the literature. Ultimately, these findings help pave the path toward the development of a truly high-yield, sensitive, stable, and robust electrical biosensing platform.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.2c04098>.

Comparison of leakage currents and on/off-current ratios for various SU-8 soft-bake conditions (Figure S1); optical and electron microscopy images of Cr/Pd metal contacts under various SU-8 conditions (Figure S2); profilometry measurements of Cr/Pd metal contacts under various SU-8 conditions (Figure S3); subthreshold curves of representative solution-gated devices from each passivation condition plotted on one graph (Figure S4); performance comparison of SU-8 + HfO_2 devices made with 8 and 30 nm HfO_2 dielectric thicknesses (Figure S5); and chemical verification of successful deposition of a final PEG polymer layer (Figure S6) (PDF)

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Author Contributions

F.M.A., N.X.W., and A.D.F. conceived the study. F.M.A. fabricated and tested the devices and analyzed the data. N.X.W. contributed to experimental design, including fabrication and testing processes, and figure design. S.L. aided in printing optimization. J.L.D. contributed to the device design. A.D.F. supervised the research and provided scientific guidance. F.M.A. and A.D.F. wrote the manuscript with revision and approval from all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

All authors gratefully acknowledge support from the National Institutes of Health (NIH) under Award No. 1R01HL146849. The content presented in this manuscript represents the views of the authors and does not necessarily represent the views of the funding organizations.

ABBREVIATIONS

AJP, aerosol jet printing
 ALD, atomic layer deposition
 BioFET, biosensor field-effect transistor
 CNT, carbon nanotube
 CNT-TFT, carbon nanotube thin-film transistor
 ELISA, enzyme-linked immunosorbent assay
 PBS, phosphate buffered saline
 PEG, poly(ethylene glycol)
 UV, ultraviolet
 RTA, rapid thermal annealing
 SB, soft-bake
 SEM, scanning electron microscopy
 SS, subthreshold swing
 XPS, X-ray photoelectron spectroscopy

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