

Low-voltage Flexible OFETs with Gelatin Gate Dielectric

The development of low-voltage operated OFETs has gained significant interest across several applications, including biomedical sensors, RFIDs, and wearable, and stretchable technology due to the need for low-power consumption and the limitation of battery capacity in wearable devices. Over the past few decades, numerous efforts have been dedicated to minimizing the operating voltage of OFETs while maintaining high performance, which is a prerequisite for real-world applications. Out of all the major components of OFETs, the gate dielectric layer is one of the crucial components that significantly influences the operating voltage, operational stability, and performance of the device. Low-voltage operation can be attributed by increasing the gate dielectric capacitance density (C_i), lowering the trap density in the bulk of semiconductors, and improving the interfaces between semiconductor/dielectric and electrode/semiconductor. High- k inorganic dielectrics are demonstrated in OFETs to instill high C_i , however, they are limited due to their brittle nature and the requirement of high processing temperature, which is not feasible for flexible electronics. The use of polymer electrolytes composed of mobile ions is an attractive choice for gate dielectrics to realize low-voltage OFETs. Under the influence of the gate electric field, significantly high C_i is obtained as a result of the formation of an electrical double layer (EDL) at the interface between the electrolyte and semiconductor, which is a crucial aspect for low-voltage OFETs. In this chapter, low-voltage flexible OFETs are discussed using gelatin gate dielectric with TIPS-Pentacene: PS as an active layer (Konwar, Saxena, Raghuwanshi, et al., 2022b).

4.1 INTRODUCTION

Gelatin is one of the most widely explored water-soluble natural proteins, showing excellent biocompatibility, biodegradability, and nontoxicity suitable for fabrication of devices for green electronics. It is primarily derived from animal bone and skin and a hydrogel, a three-dimensional network structure containing a considerable quantity of water that is created by crosslinking hydrophilic polymer chains in water, resulting in good deformation ability (Yuk et al., 2019). The gelatin hydrogel provides an ultra-smooth surface with high capacitance density and it has been already utilized as a potential electrolyte in wearable electronics, biomedical diagnostics, and health monitoring (He et al., 2016; Lai et al., 2019; Mandal et al., 2020b; Mao et al., 2013). At higher humidity, gelatin film provides efficient transistor performances due to its moisture-loving nature (Mandal et al., 2020a). Hence, gelatin is a very suitable candidate for exploration in high-performance OFET devices. Apart from eco-friendliness, low voltage operated devices are essential due to low power requirements in various applications. Though there are various reports for flexible OFET devices exhibiting high field-effect mobility values higher than $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, most of them are for higher operating voltages (He et al., 2016; Mao et al., 2013; Cong Wang et al., 2020). Newer materials and processes are explored for OFETs to achieve high performance along with low voltage operation with low threshold voltage (V_{TH}) ideally near 0 V and a low subthreshold swing (SS) values (Guo et al., 2021; Mandal et al., 2020a; Nikolka et al., 2020). The performance of OFET is highly controlled by the properties of dielectric materials, the quality of the active layer, and the density of charge trapped at the dielectric: semiconductor interface (Riera-Galindo et al., 2019). OFETs operating at low voltages have been demonstrated with various crosslinked polymer and polymer blends, self-assembled mono and multi-layers (SAMs),

high-k inorganic, and ion-based polyelectrolytes or biopolymers (Kwon et al., 2020; Patrikar et al., 2021; S. Rahi et al., 2022; Y. Wang et al., 2019), however, very few of them are demonstrated for flexible substrates. In addition, organic semiconductors are crucial components for tuning the device performance for example the blend of organic semiconductor and polymer has resulted in high performance and stability in OFET devices due to an enhanced quality of dielectric: semiconductor interface through vertical phase separation (Afraj et al., 2021; Janasz et al., 2021; Riera-Galindo et al., 2019). However, attaining electrical and operational stability under various circumstances is another challenge for organic devices as the performance parameters are easily affected by the environment and applied strain (Chen et al., 2021). Stability in the performance of OFETs is achieved by various steps such as interface engineering and utilization of air-stable organic semiconductors in device fabrication (Nair et al., 2016; Subbarao et al., 2015). It is important to note that high-performance, low-voltage operated, and reliable OFET devices with high electromechanical and environmental stability are essential for real-life systems.

In this chapter, water-soluble natural protein gelatin is explored as a gate dielectric for the demonstration of high-performance and low voltage (-3V) operation in flexible OFETs. The fabricated p-channel devices showed excellent electrical characteristics and $\mu_{\max}$ up to $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, high $I_{\text{on}}/I_{\text{off}}$ ratio, low SS, and nearly zero V_{TH} due to the high-quality dielectric semiconductor interface achieved through optimized processes of fabricating flexible OFET devices. High operational stability was exhibited, performing various stability experiments of bias-stress, repeatability, electromechanical stability, cyclic stability, and long-term ambient stability. For electromechanical stability, no significant changes in the performance were observed upon application of compressive and tensile strain due to bending. Exceptional environmental stability was obtained, with almost constant electrical performance maintained for a duration of 24 weeks. The applicability of the circuit was further analyzed through the switching characteristics of resistive load inverters.

4.2 EXPERIMENTATION

The schematic of the flexible OFET device and the optical picture of the fabricated devices are shown in Figure 4.1 (a) and (b) respectively. OFET devices were fabricated in bottom gate top contact architecture on ITO coated flexible PET substrate.

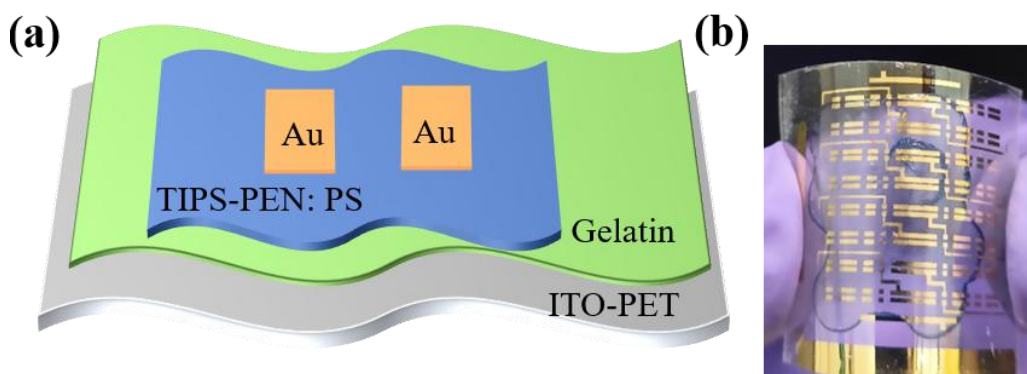


Figure 4.1 : Schematic of flexible OFET device with gelatin as gate dielectric. (b) Picture of fabricated array of transistors.

The substrate was thoroughly cleaned as discussed in Chapter 2 (section 2.1) before using for fabrication. All materials were purchased from Sigma Aldrich and used for device fabrication without any purification. To prepare the gelatin film, 300-bloom type-A gelatin was dissolved in deionized water (DI) with a concentration of 10 wt. % at 60°C for 2.5 hours, followed by spin-coating at 2000 rpm for 60 s and further annealed for 36 hours at 50°C . To form the blend solution of the active layer; 0.5 wt. % solutions of TIPS-Pentacene and PS ($mw = 28,000$) were prepared in toluene separately by stirring for 2.5 hours at 65°C . Both the solutions were mixed in equal amounts at 1:1 ratio and stirred for another 1 hour at the same 65°C temperature. This solution was deposited over gelatin surface by drop-casting. Both the dielectric and active layer thickness were measured by Dektak XT surface profiler from Bruker and found to be $\sim 520 \text{ nm}$ and $\sim 1 \mu\text{m}$

respectively. Finally, the gold (Au) source/drain top contacts were deposited through a shadow mask by thermal evaporation with a base vacuum of 10^{-6} torr. All the devices were characterized using Keithley 4200 SCS analyzer in normal ambient conditions.

All crucial electrical parameters including μ and V_{TH} were calculated from the highest slope of linear fit $(I_{DS})^{1/2}$ vs. V_{GS} plot from transfer characteristics in saturation region using the standard saturation regime drain current formula. Gate capacitance (C_i) per unit area is measured through MIS structure at the lowest possible frequency of 1 kHz and an average value of $7.0 (\pm 0.2)$ nF/cm² was found. In general, C_i values measured at lower frequencies are preferred for natural polymer-based gate dielectrics to prevent overestimation of charge carrier mobility. However, due to the measurement limitations of the Keithley 4200 SCS parameter analyzer, the capacitance in this study was determined at an available frequency of 1 kHz.

4.3 RESULTS AND DISCUSSION

4.3.1 Surface Morphology

The surface morphology of various films was studied by atomic force microscopy (scanning probe microscopy (SPM) XE-70 AFM system from Park Systems). AFM image of gelatin film showing a uniform morphology is given in Figure 4.2 (a). A smooth dielectric surface with root mean square (RMS) surface roughness of 0.6 ± 0.4 nm was obtained, indicating the excellent quality of dielectric film. Reduced surface roughness is desirable to reduce the inconsistencies at the dielectric/semiconductor interface and supports high-quality semiconductor growth and interface with semiconductors. On the contrary, poor-quality semiconductor growth can result in a large number of charge-trapping sites. Figure 4.2 (b) shows XRD pattern of TIPS-Pentacene: PS film. As it can be observed, a highly crystalline film in the direction of (001) plane with a minimum full width half maximum (FWHM) value of 0.65 was obtained on the top of gelatin layer. A lower value of FWHM is indicative of higher crystallinity of materials. Both these surface morphology and material characterization results indicate better dielectric and semiconductor films suitable for yielding high-performance in eventual devices.

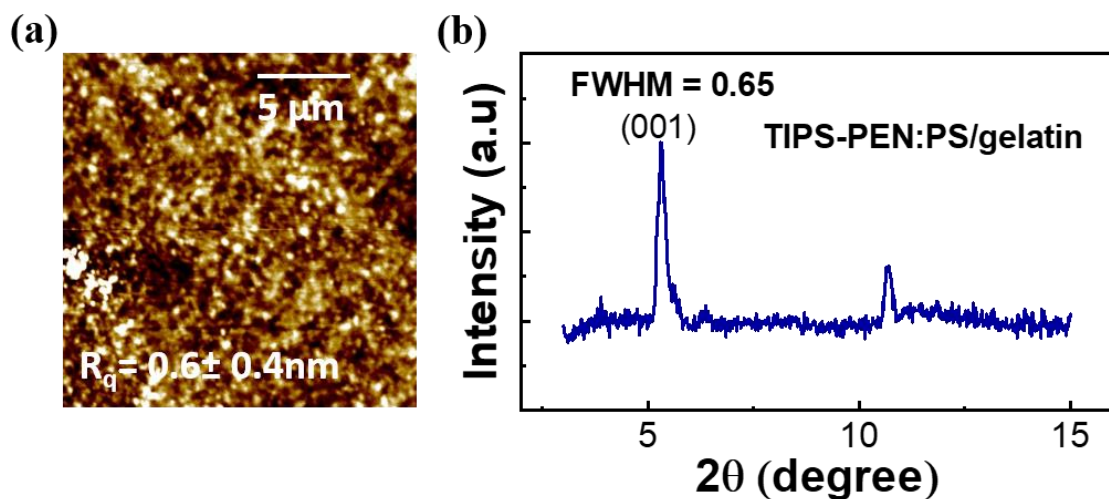


Figure 4.2 : (a) AFM image of gelatin dielectric surface, and (c) XRD pattern of TIPS-pentacene: PS exhibiting typical crystalline nature of semiconductor.

4.3.2 Electrical Performance of Flexible OFETs

The operation of fabricated devices was examined from the transfer and output characteristics. As can be seen in Figure 4.3 (a) & (b), ideal electrical characteristics was observed for the p-channel transistor operation with excellent saturation in output characteristics at -3V, which is mostly not seen for devices with gelatin. This excellent characteristic with very low voltage operation at -3 V is attributed to the combined properties of gate dielectric and semiconductors. The gelatin hydrogel consists of polymer networks and mobile ions formed by cross-linking of hydrophilic polymer chains. Under the influence of an external field, the mobile

ions migrate towards electrodes forming EDLs at the dielectric/semiconductor and dielectric/gate electrode interfaces (Mandal et al., 2020a). As a result of this phenomenon, a high EDL capacitance density is obtained, which lowers the device's driving voltage (Lai et al., 2019). The PS polymer layer formed between gelatin and organic semiconductor through vertical-phase separation avoids the direct interaction between charge carriers and functional groups present in biopolymers and reduces overall gate leakage current challenge (Bharti et al., 2016; Raghuwanshi et al., 2018). The performance parameters were extracted from transfer characteristics of all the devices as mentioned earlier. A high value of μ with average and maximum values of 1.6 ± 0.5 and $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved and summarized for 15 devices from a batch. Statistical distribution of mobility for these devices of a substrate is given in Figure 4.3 (c).

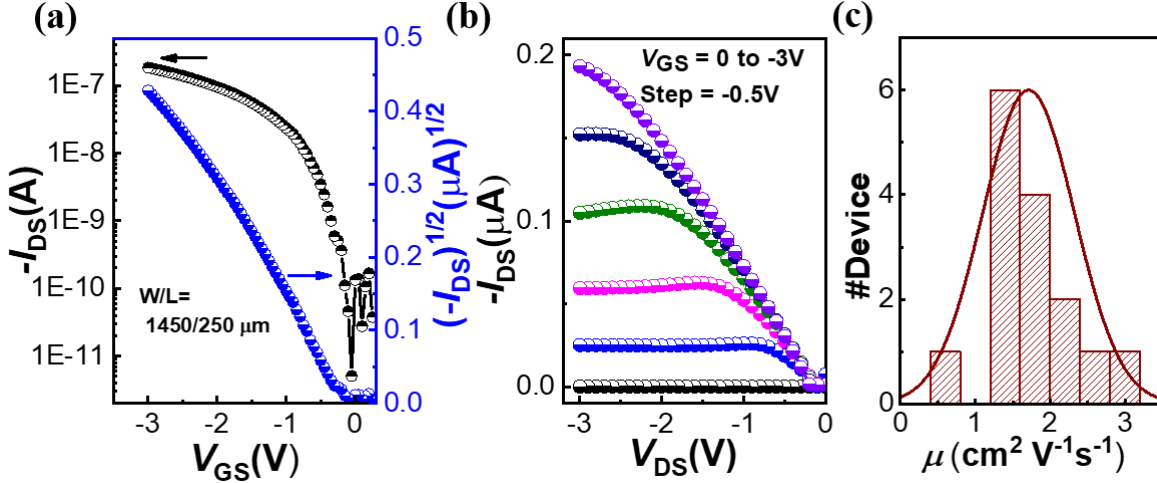


Figure 4.3 : (a) Transfer, and (b) output characteristics of a low-voltage operated p-channel OFET device with gelatin biopolymer as gate dielectric layer. (c) Statistical distribution of mobility for 15 OFET devices on a substrate.

As it can be seen from this distribution, most of the devices exhibit μ near $1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for C_i value measured at 1 kHz. Moreover, a very small hysteresis was observed in electrical characteristics. In general, hysteresis is expected in polymer dielectrics (Ling et al., 2019). Further, the resulting bilayer gate dielectrics (gelatin:PS in this case) cause vertical phase separation from hydrophilic interface to hydrophobic interface adjoining to organic semiconductors well, leading to reduced hysteresis and improved stability in OFET devices (Yin et al., 2018). These high numbers for devices operating at very low voltage and exhibiting ideal characteristics with excellent saturation in output curves are indeed remarkable and rare to achieve. A high I_{on}/I_{off} on the order of 10^4 was achieved. Moreover, a near-zero average V_{TH} of $-0.2 \pm 0.04 \text{ V}$ was achieved, making these devices suitable for further lowering of operating voltages. The SS of about 250 mV/dec indicated a very high-quality interface for solution-processed devices and it further confirms sub 3V operation with steep switching. Lower SS values in the range of 100 to 250 mV are reported for flexible OFET devices, however, these are mostly with vacuum-evaporated semiconductors (Bisoyi et al., 2014). A very low average value for D_{it} of $1.4 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ was achieved indicating excellent transistor properties with natural protein gate dielectric.

4.3.3 Investigation of Electrical and Operational Stability: Effect of Bending

Figure 4.4 summarizes the effect of bending on transistor performance for the application of both tensile and compressive strain. To study this, the fabricated samples were mounted on a curved surface with constant bending radius (R_{bend}) of 12.5 mm, 7 mm, and 5 mm. The devices were subjected to both tensile and compressive strains for 15 minutes for one static cycle, and their transistor performance was evaluated after being released from the bent state. The corresponding strain rates can be calculated by using the standard formula and found to be 0.5, 0.84, and 1.27%, respectively (Sachin Rahi et al., 2022). Figure 4.4 (a) and (b) respectively show the images of the application of both tensile and compressive strain with R_{bend} of 12.5 mm. Plots of

the transfer characteristics for unbent and the devices with bending under tensile and compressive strain are shown in Figure 4.4 (c). Significantly stable characteristics with negligible changes are observed for both types of applied strain on the devices. In addition, bias-stress stability of OFET devices for a constant bias of $V_{DS} = V_{GS} = -3V$ was studied. Figure 4.4 (d) shows the plot of normalized I_{DS} during the stress period for 1 hour. As expected, a typical gradual decay of I_{DS} is observed with time due to charge trapping at the dielectric/semiconductor interface (Raghuwanshi et al., 2019). For an unbent device, a low decay of 15% was observed affirming high stability in the devices under bias stress. Similarly, ~17% and ~18% decay were shown for the devices after application of tensile and compressive strain. Overall, this decay is due to combined effect of mechanical strain and bias-stress indicating a high degree of charge trapping at interfaces. Also, the generation of micro-defects/cracks in the devices leads toward higher drain current decay (Bharti et al., 2016). For these flexible devices with gelatin dielectric, the bias-stress induced decay in I_{DS} was less than 20%, which indicates very high electromechanical stability. Gelatin provides high mechanical robustness and high elongation properties of films under various strains (Yuk et al., 2019), making it a suitable candidate for dielectric in flexible devices. Moreover, as reported earlier, the blending with PS also assists in suppressing the effects of mechanical deformation on devices (Raghuwanshi et al., 2018). Devices were further bent at R_{bend} of 7.5 mm and 5 mm for both tensile and compressive strain to study their electrical performances. The average value of μ and V_{TH} with standard deviation in both cases are shown in Figure 4.4 (e) and (f). Average μ varies from 1.5 to 1.2 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, and 1.4 to 1 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, for tensile and compressive strain respectively. Repeated bending can induce the formation of cracks in the dielectric and semiconductor layers, leading to alterations in film morphology, affecting the overall transistor performance.

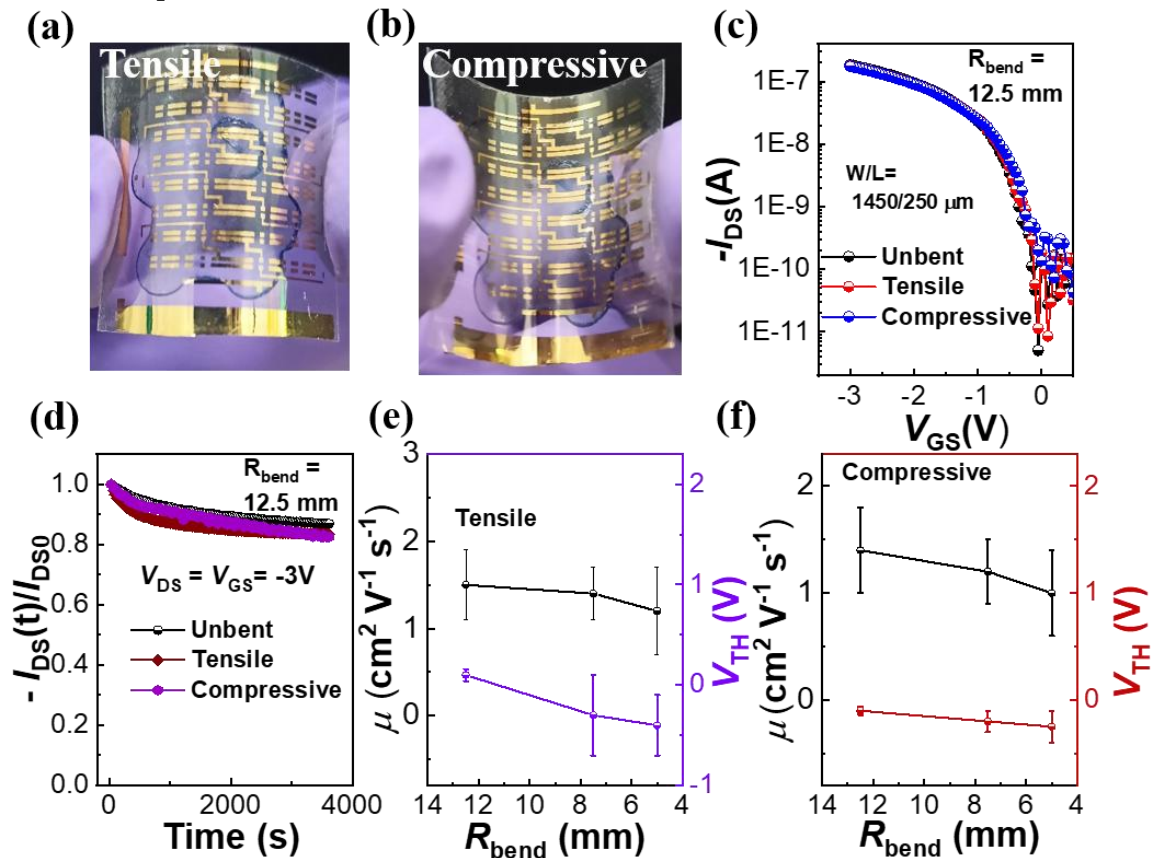


Figure 4.4 : (a) Tensile, and (b) compressive bending strategy for the fabricated devices. (c) Transfer characteristics for unbent and under different bending conditions and (d) Normalized I_{DS} decay with time after application of bias-stress for various bending conditions for R_{bend} of 12.5 mm. Variation of performance parameters μ and V_{TH} with decreasing R_{bend} from 12.5 to 5 mm for tensile (e), and compressive (f) strain.

Table 4.1 : Summary of calculated electrical parameters for pristine and different bending devices for R_{bend} of 12.5 mm.

Device	μ_{avg} (cm^2/Vs)	μ_{max} (cm^2/Vs)	V_{TH} (V)	$I_{\text{on}}/I_{\text{off}}$	SS (V/dec)	D_{it} ($10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)
Pristine	1.6 ± 0.5	3.0	-0.2 ± 0.04	$\sim 10^4$	0.25	1.4
Tensile	1.5 ± 0.5	2.4	-0.1 ± 0.06	$\sim 10^4$	0.27	1.5
Compress.	1.4 ± 0.4	2.2	-0.05 ± 0.04	$\sim 10^3$	0.37	1.3

Multiple scanning of transfer characteristics was performed to study the repeatability of fabricated devices. Figure 4.5 (a) and (b) show the multiple transfer curves for repeatability for 100 cycles and corresponding change in I_{DS} and V_{TH} at different cycles respectively for an unbent device. Excellent electrical stability with negligible variations in I_{DS} and V_{TH} , were achieved throughout the scanning period confirming the high electrical stability. Figure 4.5 (c) & (e) represent the repeatability plots of devices with tensile and compressive bending. Figure 3.6 (d) & (f) show the corresponding extracted values of I_{DS} and V_{TH} . For both the cases, almost overlapping transfer curves were achieved, with a highly stable I_{DS} and small change in V_{TH} . Summary of all the crucial performance parameters extracted and calculated for each condition is given in Table 4.1. Remarkably high mobility was maintained even after bending in both directions, with a small variation from 1.6 to $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 3.0 to $2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively in average and maximum values for unbent to bent conditions.

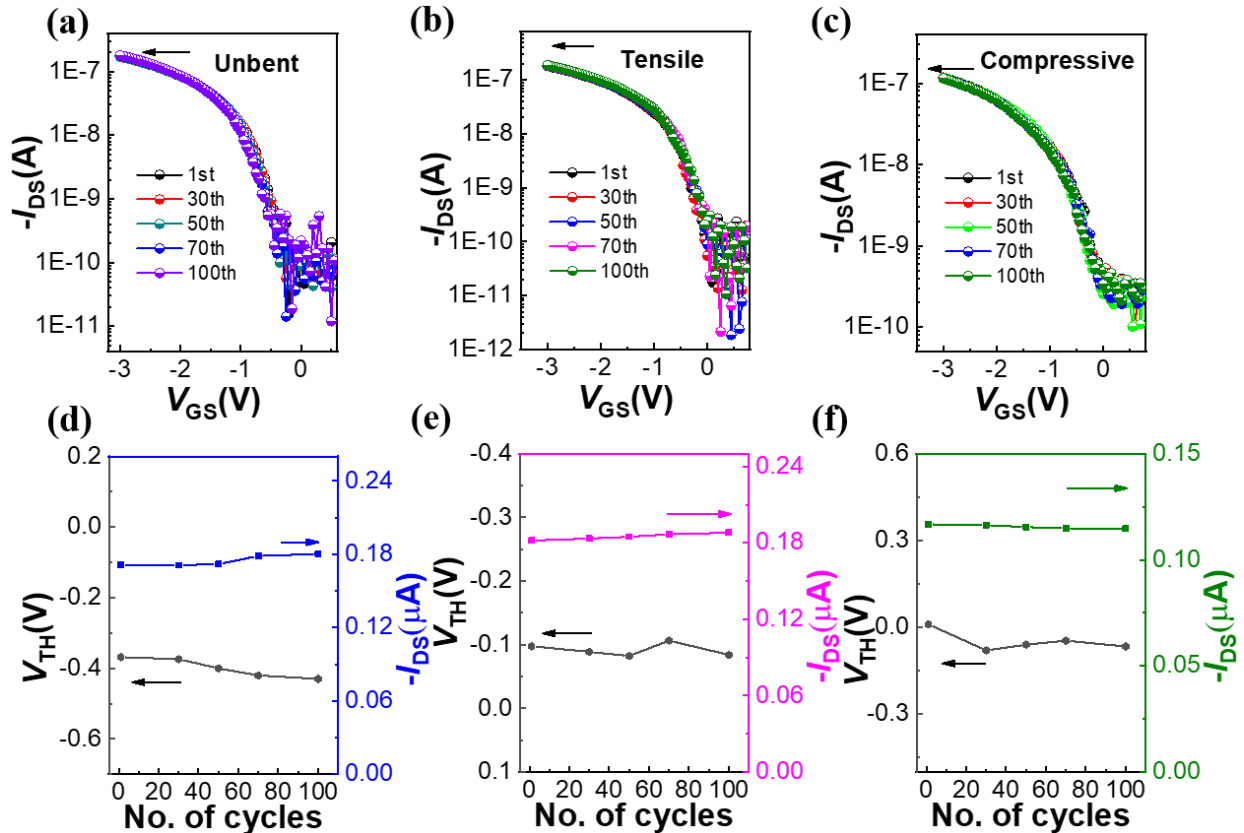


Figure 4.5 : Multiple scanning of transfer characteristics upto 100 cycles and respective changes in I_{DS} and V_{TH} over the scan period for pristine device (a) & (b); under tensile bending (c) & (d); and under compressive bending (e) & (f).

4.3.4 Cyclic and Environmental Stability

To further investigate the operational reliability of these devices, a cyclic stability study was performed. For the same, continuous input pulses were applied on gate terminal between in the range of -3 V and 3 V over a period of time and for certain number of cycles. Figure 4.6 (a) and (b) show the corresponding continuous variation of I_{DS} with time and the I_{DS} values at on and off states for 120 cycles. Moreover, the long-term and environmental stability of devices was

investigated over 24 weeks with devices kept in normal lab ambient with relative humidity fluctuating between 45-65%, with maintain a relatively stable temperature within the range of 30-40 °C. The transfer characteristics for pristine, 10 weeks, and 24 weeks for a particular device are shown in Figure 4.6 (c). Corresponding V_{TH} and μ values are plotted in Figure 4.6 (d). As it can be seen from these results, the device performance was highly stable even after keeping the devices in normal ambient conditions for such a long duration. One possible reason for this could be the high degree of plasticity of gelatin film under atmospheric conditions for a longer period facilitating air stable devices (Chang et al., 2019). The hydrophobic nature of PS binder also resists further interface degradations while forming a high-quality uniform dielectric/semiconductor interface (Bharti et al., 2016). These robust properties lead the devices to be used in reliable circuit as well as real-time sensing applications where stability of the performance of reference devices is essential.

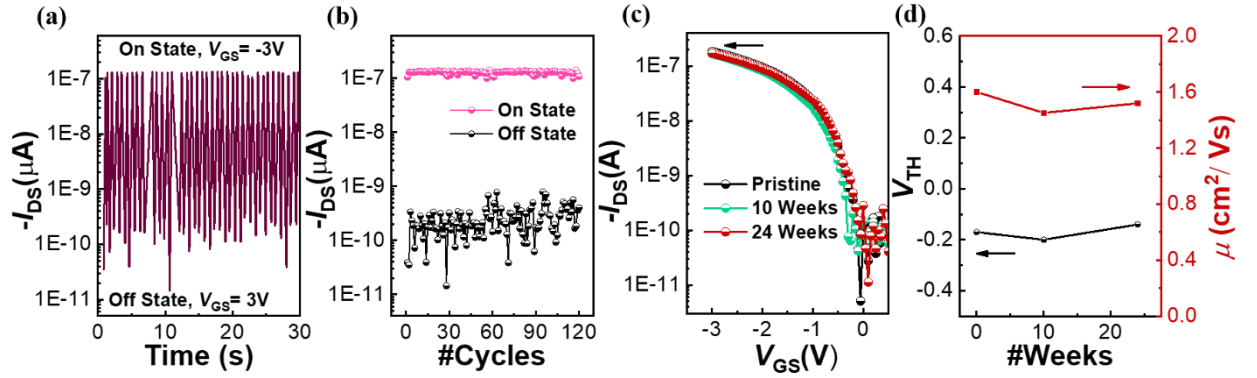


Figure 4.6 : Cyclic stability for on/off switching between $V_{GS} = -3V$ and $V_{GS} = 3V$ at $V_{GS} = -3V$ with time (a), and number of cycles (b). Demonstration of long-term stability through transfer characteristics for 24 weeks (c), and corresponding variation of V_{TH} and μ for this time period (d).

4.3.5 Resistive-Load Inverter

The fabricated OFETs were further investigated for circuit applicability by using them in resistive load inverter circuits as shown in Figure 4.7 (a). External load resistance ranging from 10 to 40 M Ω was connected with the OFET devices.

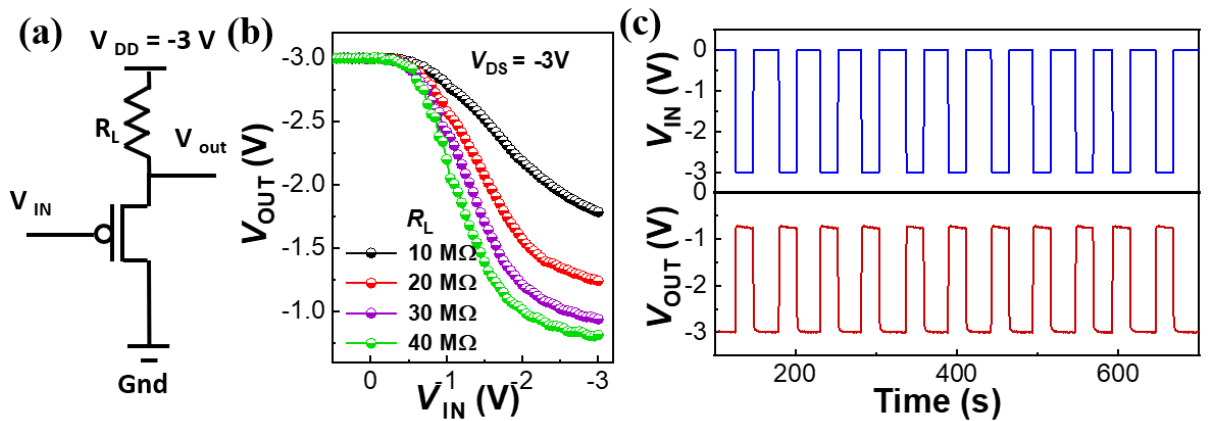


Figure 4.7 : (a) Resistive load inverter circuit used for OFET devices. (b) Voltage transfer characteristics at different load resistance values, and (c) dynamic response for 40 M Ω load resistance.

Input voltage sweep between 0 to -3 V was applied at the gate terminal corresponding output voltage responses at different resistance values were studied. Typical voltage transfer characteristics with various R_L values are shown in Figure 4.7 (b), exhibiting proper voltage inversion for -3V operation. The output voltage (V_{OUT}) was almost equal to the supply voltage -3V at low input voltage (V_{IN}), indicating that the p-type OFET was completely turned off. As V_{IN} increased and eventually exceeded the inverter switching threshold, the p-type OFET was turned

on and V_{OUT} dropped to a low value. A relatively perfect high state or logic 1 state occurs for low input and low state or logic 0 state is obtained for high input. The transfer behavior is more prominent for high resistance values because of the considerable voltage drop across the resistance. Time-resolved dynamic response was demonstrated with a load resistance of 40 M Ω on applying a square wave pulses input between 0 and -3V at the gate terminal and shown in Figure 4.7 (c). These results demonstrate the suitability of gelatin as an excellent dielectric candidate for circuit applications for eco-sustainable electronics.

4.4 CONCLUSION

In this chapter, high-performance OFET devices based on water-soluble gelatin biopolymer gate dielectric were demonstrated. Fabricated devices were operated at a low voltage of -3 V with excellent p-channel characteristics. Remarkably high values of maximum and average μ of 3.0 cm² V⁻¹ s⁻¹ and 1.6 $\pm$ 0.5 cm² V⁻¹ s⁻¹ were achieved respectively along with V_{TH} of near 0 V. Further, excellent electrical and operational stability was observed through various multiple scanning of transfer characteristics, bias-stress, cyclic stability, and long-term and environmental stability studies. High electromechanical stability was attained by combining the effect of bending through both the tensile and compressive strain. Finally, the resistive load-based inverter circuits were demonstrated with these devices using external load resistances. Our results indicate that gelatin has the potential to be used as a suitable gate dielectric for future smart, disposable, and green electronics.