

Fully Transparent Field-Effect Biosensors

X. Du^{*}, Y. Li^{**}, and G. S. Herman^{*}

^{*}Oregon State University, Corvallis, OR, USA, Greg.Herman@oregonstate.edu

^{**}Civil Aviation University of China, Tianjin, China, yj-li@cauc.edu.cn

ABSTRACT

High electrical and chemical stability of amorphous indium gallium oxide (IGZO) thin film transistors (TFTs) are critical for a wide range of applications. Fluorinated hexylphosphonic acid (FPA) self-assembled monolayers (SAMs) adsorbed on the backchannel of IGZO can significantly improve both electrical and chemical stability of IGZO-TFTs even in aqueous solutions. Results indicate that FPA functionalized, enzyme free IGZO-TFTs have glucose concentration-dependent changes in their electrical response. A linear relationship between logarithmic drain-source current change, turn-on voltage shift, and electrical hysteresis with respect to glucose concentration were observed. The ability to correlate glucose concentration to three different electrical responses should improve accuracy of IGZO-TFT sensors. To further improve selectivity to glucose, glucose oxidase can also be immobilized onto the IGZO-TFT backchannel surface.

Keywords: indium gallium zinc oxide, glucose sensor, transparent thin film transistor

1 INTRODUCTION

In the U.S. more than 1 million people have been diagnosed with type I diabetes mellitus. Extremes in blood glucose levels can lead to major health issues. High blood sugar (hyperglycemia) can cause complications such as macrovascular and kidney disease, while low blood sugar (hypoglycemia) can lead to seizures and loss of consciousness [1,2]. Glucose sensors are a critical component of an artificial pancreas and have been extensively studied during the past several decades [3]. For these applications the sensors need to be sensitive and reliable while measuring glucose concentrations over the normal physiological range (i.e., 2–30 mM in the interstitial fluid [4] and 0.1–0.4 mM in tear fluid [5]).

Amorphous indium gallium oxide (IGZO) thin film transistors (TFTs) can be processed at low temperatures that allow device fabrication on flexible, polymeric substrates, while retaining relatively high electron mobilities, low operating voltages, and very low off currents [6]. Furthermore, IGZO-TFTs are a promising technology that has been commercialized in displays [7,8]. We have begun to investigate the role of surface chemistry on device performance and found that self-assembled

monolayers (SAMs) can significantly improve IGZO-TFT electrical stability [9]. We have found that (3,3,4,4,5,5,6,6,6-nonafluorohexyl) phosphonic acid (FPA) SAMs adsorbed on IGZO backchannel surfaces gave the best device electrical stability compared to hexyl phosphonic acid (HPA) SAMs or bare IGZO surfaces. The improved electrical stability with the FPA SAMs can be primarily attributed to a reduction in molecular adsorption of contaminants on the IGZO backchannel surface and reduction of trapping states with phosphonic acid binding to the IGZO surface. We have recently demonstrated high sensitivity glucose sensors after functionalization of IGZO-TFT backchannel surfaces with aminosilane and glucose oxidase enzyme [10]. Glucose concentrations as low as 10 μM could be measured using nanostructured IGZO-TFTs [11]. More recently, we have demonstrated high-performance, fully-transparent IGZO-TFT based biosensors fabricated directly on highly-curved glass substrates [12]. The electrical characteristics were comparable to devices fabricated on planar surfaces, and may provide a method to develop fully transparent, highly-sensitive sensors onto catheters, optical fibers, and electrophysical/neural imaging devices.

In this study, we use FPA SAMs as molecular passivation layers on IGZO-TFT backchannel surfaces. We found that changes in the devices electrical response could be correlated with glucose concentration. For comparison, we have included data for IGZO-TFT sensors with glucose oxidase (GOx) immobilized on the backchannel surface.

2 EXPERIMENTAL

2.1 IGZO-TFT Fabrication

IGZO-TFT test structures were fabricated using a heavily p-doped Si substrate as the gate and thermally grown SiO_2 (100 nm thick) as the gate dielectric. Source and drain electrodes were patterned using a shadow mask during RF magnetron sputter deposition of ITO (~250 nm thick), 120W RF power, ~4 mTorr chamber pressure, and 20 sccm flow rate of Ar, giving a W/L ratio of 1000 $\mu\text{m}/200 \mu\text{m}$. Amorphous IGZO films (~50 nm thick) were deposited by sputtering (molar composition: $\text{In}_2\text{O}_3:\text{Ga}_2\text{O}_3:\text{ZnO}$), 100W RF power, ~4 mTorr chamber pressure, and 20 sccm flow rate with a 1:19 ($\text{O}_2:\text{Ar}$) ratio. IGZO active layers were patterned using a shadow mask

during deposition, and the films were subsequently annealed in air to 300 °C.

2.2 Backchannel Passivation

The IGZO backchannel surface was activated and cleaned using an UV-Ozone treatment for 5 minutes.

For FPA passivation, the IGZO-TFT was immediately soaked in 2mM FPA solution in 95% ethanol. After 24 hours, samples were removed from the solution, rinsed with 95% ethanol, and then dried with flowing nitrogen. The passivated TFTs were annealed at 140 °C for 48 h in flowing dry nitrogen for FPA bond activation. In order to remove physisorbed SAMs the samples were further sonicated in a 5% triethylamine/ethanol solution, rinsed with ethanol, and then dried with nitrogen.

For glucose oxidase (GOx) passivation, the IGZO-TFT was immediately soaked in a 1% aminopropyl trimethoxysilane (APTMS, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) ethanol solution for 2 hours, rinsed with ethanol, and then dried with flowing nitrogen. The APTMS-IGZO film was then immersed in 20 mM glutaraldehyde (GA, $\text{OHC}(\text{CH}_2)_3\text{CHO}$) in a phosphate buffer solution and then the device was transferred to and kept in 10 g/L GOx in PBS for 2 hours. The sample was rinsed with water and then dried with flowing nitrogen.

2.3 Electrical Characterization and Glucose Sensing

All IGZO-TFT electrical measurements were performed in the dark at room temperature using an Agilent 4155C precision semiconductor parameter analyzer. Forward (low voltage to high voltage) and backward (high voltage to low voltage) sweep drain-to-source current versus gate voltage (I_D - V_G) transfer curves were measured with the drain voltage (V_D) set to 100 mV at a V_G sweep step of 0.5 V. A PDMS well was attached to the top of the exposed IGZO channel as shown in Figure 1. Solutions were introduced into the PDMS well using a micropipette, where the glucose concentration was varied between 0-32 mM. A phosphate buffered saline (PBS) solution (composed of 137 mM NaCl, 2.5 mM KCl, 4 mM NaH_2PO_4 , and 16 mM Na_2HPO_4 , pH 7.4) was used to dilute glucose to the range of concentrations of interest.

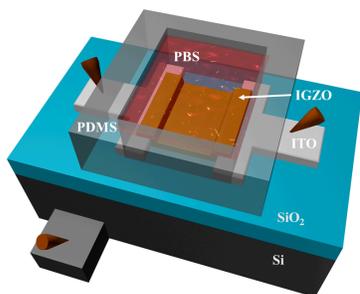


Figure 1: Schematic illustration of PDMS well on IGZO-TFT sensor.

3 RESULTS AND DISCUSSION

In Figure 2 we compare transfer characteristics of IGZO-TFTs with and without FPA passivation. These measurements were performed in air, where I_D was measured while V_G was scanned from -10 V up to 25 V and back down to -10 V with $V_D = 100$ mV. The IGZO-TFTs have good electrical characteristics and did not have significant hysteresis between the up and down sweeps of V_G in the I_D - V_G data suggesting traps are able to stay in equilibrium with the sweep rate of V_G .

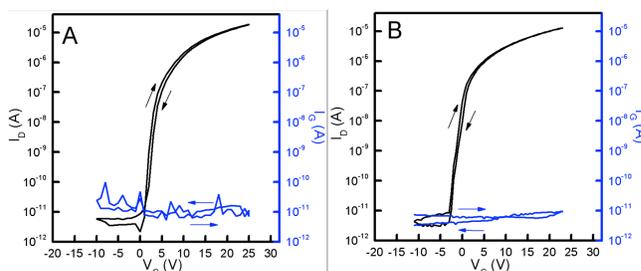


Figure 2: Transfer characteristics of TFTs with IGZO channel layer (A) without passivation and (B) with FPA passivation. ($V_D = 100$ mV).

The IGZO-TFTs have high I_{ON}/I_{OFF} ratio $\sim 10^6$, due in part to low I_{OFF} , which is very important for sensors, a high $\mu_{avg} > 4 \text{ cm}^2/\text{Vs}$, low gate leakage currents (I_G), and very low off currents. The major difference after adsorption of FPA on the back channel surface is a slight increase in μ_{avg} , which can be correlated with a decrease in V_{ON} , and a reduction in hysteresis.

Transfer characteristics are shown in Figure 3 for IGZO-TFTs with and without FPA passivation, and with varying concentration of glucose. I_{ON}/I_{OFF} ratios for the devices in solution decreased to $\sim 10^4$, primarily due to an increase in I_{OFF} . For IGZO-TFTs without passivation there was a significant increase in the hysteresis of up to ~ 17 V when the backchannel was exposed to PBS solution, and increased to more than 26 V with the addition of 30 mM glucose. For IGZO-TFTs passivated by FPA we found that the hysteresis was significantly reduced to less than 2 V in PBS solution, and only increased to ~ 3 V in 30 mM glucose. For the FPA passivated IGZO-TFTs we found that the turn on voltage shifted to negative values with increasing glucose concentration regardless of V_G sweep direction. These data indicate that the interaction of glucose with the FPA layer induces electrical conduction changes in the IGZO channel, and that these changes are dependent on glucose concentrations.

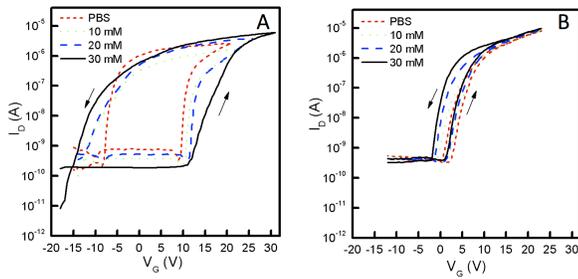


Figure 3: IGZO-TFT tested in varying concentrations of glucose (A) without passivation and (B) with FPA passivation. ($V_D = 100$ mV).

To quantify the sensor response to glucose, we measured I_D with V_G set to 5 V, which was the maximum in sub-threshold slope for the FPA passivated IGZO-TFT in PBS solution. In Figure 4 we plot I_D versus glucose concentration where the data was plotted on a linear (solid circles, left axis) and semi-log scale (open circles, right axis). Significant changes in I_D were observed in this glucose concentration range and a linear relationship was obtained for the semi-log plot. The slope of $\log(I_D)$ versus glucose concentration was 0.02 and $0.07 \text{ A}\cdot\text{mM}^{-1}$ for low-to-high and high-to-low V_G sweeps, respectively, and a coefficient of determination (R^2) of 0.999 was found for glucose concentrations up to 30 mM.

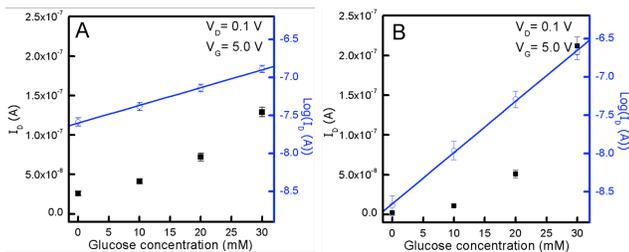


Figure 4: I_D change versus glucose concentrations using FPA passivated IGZO-TFT (A) from low voltage to high voltage and (B) from high to low voltage.

In Figure 5 we plot the change in V_{ON} versus glucose concentration and find that V_{ON} has a negative shift with increasing glucose concentration with a linear relationship for the glucose concentration range of interest. The slope of V_{ON} versus glucose concentration was determined to be -0.05 and $-0.1 \text{ V}\cdot\text{mM}^{-1}$ for low-to-high and high-to-low V_G sweeps, respectively.

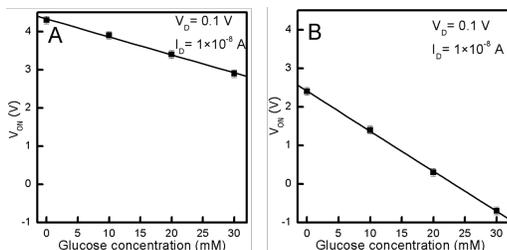


Figure 5: V_{ON} versus glucose concentration using FPA passivated IGZO-TFT (where V_{ON} was determined as the

V_G where $I_D = 1 \times 10^{-8}$ A) (A) from low voltage to high voltage and (B) from high to low voltage.

In Figure 6 we show a plot of IGZO-FET hysteresis versus glucose concentration. We found that the hysteresis of transfer curve increased linearly with respect to glucose concentration, where the slope of hysteresis versus glucose concentration was determined to be $0.03 \text{ V}\cdot\text{mM}^{-1}$. These data suggest that several complimentary electrical measurements allow glucose concentrations to be determined, and the combination of measuring I_D at a fixed gate voltage, V_{ON} shifts, and device hysteresis may allow improved accuracy for sensing of glucose.

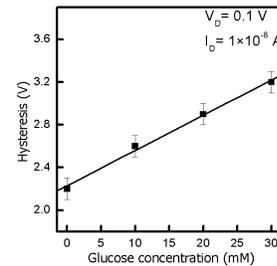


Figure 6: Hysteresis versus glucose concentration using FPA passivated IGZO-TFT.

To illustrate the stability of the IGZO-TFTs we measured the transfer characteristics after removal from the glucose solutions, and after the surface was allowed to dry. Irrespective of surface treatment the major changes were a decrease in mobility and I_{ON}/I_{OFF} , and an increase in hysteresis compared to devices prior to testing in PBS/glucose solutions. The FPA passivated IGZO-TFTs had a relatively smaller change between before and after measurements, suggesting improved chemical stability of the backchannel interface. The gate leakage current was still very low, suggesting no incorporation of ions in the dielectric during testing in aqueous media.

To quantify the the GOx functionalized, nanostructured IGZO-TFT sensor we measured I_D with V_G set to the maximum in sub-threshold slope ($V_G = 11$ V) for the IGZO-FET in PBS solution. In Figure 7 we show the continuous monitoring of ΔI_D versus glucose concentration (C_{glucose}) when a buffered solution flows over the device. Significant changes in ΔI_D were observed for changes in the glucose concentration, where ΔI_D decreases/increases in a stepwise fashion as C_{glucose} increased/decreased, respectively. The sensor response time was less than 10 s. The arrows in Figure 7 indicate when acetaminophen and ascorbic acid (interfering compounds) were added to the electrolyte at the end of the experiment.

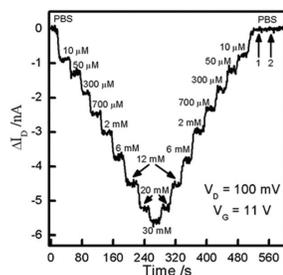


Figure 7: Measurement of ΔI_D for a GOx-functionalized IGZO-TFTs in PBS for varying glucose concentrations.

4 SUMMARY

In summary, we have demonstrated that IGZO-TFTs show promise as glucose sensors. Highly stable IGZO-TFTs in aqueous media were fabricated by molecular passivation of the oxide backchannel surface with FPA. The negative shift of V_{ON} and hysteresis increase in the transfer curve of FPA passivated IGZO-TFTs were proportional to glucose concentrations over the normal range typically found in patients with diabetes. A linear relationship between logarithmic I_D and glucose concentration has been observed for the FPA passivated IGZO-TFTs. GOx functionalized, nanoscale IGZO-TFT sensors were able to detect glucose concentrations as low as 10 μ M. This study advances the development of oxide-based FETs for application to glucose biosensors.

5 ACKNOWLEDGEMENTS

X. Du acknowledges funding support from the Juvenile Diabetes Research Foundation (3-PDF-2014-113-A-N). Y.L. acknowledges the support of China Scholarship Council and the Science Foundation of Civil Aviation University of China (3122013k006). This work was performed in part at the Northwest Nanotechnology Infrastructure, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542101).

REFERENCES

- [1] R. Mauseth, Y. Wang, E. Dassau, R. Kircher, D. Matheson, H. Zisser, L. Jovanovič, F. J. Doyle, J. Diabetes Sci. Technol. 4, 913 (2010).
- [2] H. Lee, B. A. Buckingham, D. M. Wilson, B. W. Bequette, J. Diabetes Sci. Technol. 3, 1082 (2009).
- [3] J. Wang, Chem. Rev. 108, 814 (2007).
- [4] S. P. Nichols, A. Koh, W. L. Storm, J. H. Shin, M. H. Schoenfisch, Chem. Rev. 113, 2528 (2013).
- [5] J. Zhang, W. Hodge, C. Hutnick, X. Wang, J. Diabetes Sci. Technol. 5, 166 (2011).
- [6] J. F. Wager, Inform. Display 32, 16 (2016).
- [7] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Nature 432, 488 (2004).
- [8] R. L. Hoffman, G. S. Herman, P. P. Mardilovich, Semiconductor Device, US 7,297,977.

- [9] X. Du, B. T. Flynn, J. R. Motley, W. F. Stickle, H. Bluhm, G. S. Herman, ECS J. Solid State Sci. Technol. 3, Q3045 (2014).
- [10] X. Du, Y. Li, J. Motley, W. F. Stickle, G. S. Herman, ACS Appl. Mater. Interfaces 8, 7631 (2016).
- [11] X. Du, Y. Li, G. S. Herman, Nanoscale 8, 18469 (2016).
- [12] X. Du, G. S. Herman, (submitted).