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pH Sensor Based on Dual Gate Organic Field Effect Transistor

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ABSTRACT– Nowadays, Organic semiconductors (OSCs) are receiving increasing attention these days because they have many attractive properties – including light weight, low-cost production, low- temperature processing, mechanical flexibility, and abundant availability. Earlier, ISFET (The ion sensitive field effect transistor) was used as a sensing device. It is used in measuring ion concentrationin the solution. It is based on inorganic field effect transistors where an electrolyte solution and ion- sensitive membrane is embedded. It is a special type of MOSFET in which gate electrode was replaved by refrence electrode and ion-sensistive layer. There are various categories of ISFET such as PH-ISFET, CHEM-ISFET, BIO-ISEFT etc. As these devices have many advantages,they show good compatibility with the CMOS technology ,controlling process very precisely,operates at equilibrium conditions,capable of showing label free detection and easy to use, still these devices suffer from few innate deficiency.In case of long-term use they are unrelible , unstable due to ionic damage and shouldhave low SNR. For sensing purpose, the main principle involves a variation in the surface capacity that occurs due to ionic interactions at the electrolye/gate oxide. ISFET main constraint lies in the the poor sensing margin within the Nernstian limit (59 mV per pH) at room temperature and this has gained much research attention over the past few decades.So,diffedrent devices have been tried till now to improve the sensing margin(>59 mV per pH) and hence this results in different device design with different configurations .We also proceeded our work with the same aim to improve the Nernestian limit using Organic Field Effect Transistor as device and hence tried different configurations to get the desired results.In our work, we have developed a dual gate organic field effect transistor (DG-OFET) based pH sensor that will be able to detect the variations in the aqueous (electrolyte) medium.In this structure source sided underlap technique with dual gate sensing approach has been used.The simulationresults were extracted with the help of software package Silvaco TCAD-ATLAS.The simulated results display that the proposed DG-OFET shows significantly higher sensitivity for different dielectrics.

KEYWORDS – ISFET, Organic Field Effect Transistors, DG-OFET, Nernestian Limit

I. INTRODUCTION

Organic semiconducting materials are posited to offer a choice for next-generation electronics in terms of facile processing and novel substrate integration for a variety of applications related to photovoltaics (PV), lighting, and sensing. It has been found that among various types of OTFTs, organic filed effect Transistors (OFETs) have been intensively investigated since they are basic elements of electronics, which have many applications like flexible active matrix displays, radio frequency identification (RFID) tags, efficient sensors and optoelectronic devices. An OFET-based sensor normally has high sensitivity because the device is the combination of a sensor and an amplifier, in which a small change of the effective gate voltage induced by analyte may lead to a pronounced variation of channel current.

Hence the pH sensors based on OFET have many advantages, including high sensitivity, feasibility for miniaturization, high throughput sensing, etc. It has been recognized that OFET-based sensors have a broad range of applications, such as pH sensing, light sensing, artificial skin, environmental monitoring, food safety detection, drug delivery and medical diagnostics. More importantly, OFETs can be used in flexible and disposable sensors. Due to these reasons, OFETs have been found to be one of the most popular research topics in recent decades and expected to have wide applications in future from flexible displays to high performance disposable.

II. LITERATURE REVIEW

MacDiarmid, et. al [1] studied most of the biological and chemical reactions,pH value is considered to be the most important parameter.The requirement of pH measurement is mostly employed in laboratories,environmentalor industry monitoring.For the measurement of hydrogen ion concentration in solutions a glass electrode which comporise of proton permeable property is the most common scheme used.Cremer in 1906 reported this detection method and this method provides high accuracy and stability but this detection system is rather expensive its maintenance is a bit timely.Thus, this led to study the ion-sensitive field effect transistor (ISFET) based ph sensor in order to reduce cost and maintenance issues somehow.

MacDiarmid, et. al [2] describe a numerical simulation appoach in order to study the pH change in electrolyte of ion-sensitive field effect transistor (ISFET) structure using

Silvaco technology computer aided design(TCAD) tool.The modelling method is manipulated by causing change in the surface potential charge depending on the electrolyte pH change and then realizing the threshold voltage shift of ISFET device and other transfer characteristic parameters.In order to define the electrolyte behaviour user-defined material properties ofered by silvaco are used.Parameters of semiconductor material such as energy bandgap, permittivity, affinity, and density of states are choosen to recreate an electrolyte solution and the area is inspected by providing numerical simulation. The suggested model permits accurate and efficient ISFET modeling by trying various designs and further optimization with commercial Silvaco TCAD tools than expensive fabrication methods.

Vanslyke, S. A, et.al [3] there are very less scientific literature available that will show OFET based realization of pH sensors, mostly ISFET-like structures are available as sensors, where the deposition of solution lies on the top of the dielectric and a counter-electrode of Ag/AgCl,must be ascend into it in order to turn on and bias the transistor.A.caboni used slightly different approach to detect pH changes in chemical solution where the sensing layer is seperated from the organic transistor completely and the gate is left floating .The transistor is stimulated by acting on a control gate capacitive coupled to the actual gate hence structure does not require Ag/Agcl electrode.Sensing is done by placing chemical species over the probe area.The immobilization of the charge on the floating gate generates an electric field and hence causes charge seperation inside the electrode,thereby affecting the channel formation in the semiconductor.This can be descibed in terms of the effective threshold voltage of the OFET.Results are obtained by making the sensor work as an ion-sensitive device .

Gymer, et.al [4] described the another structure in which analytical modelling has been carried out in junctionless Silicon on insulator ISFET for the purpose of ph sensing.In this structure whenever change in Hydrogen ion concentration occurs that is determined by pH sensor and the realization of the electrolyte region has been done by considering intrinsic semiconductor along with some variations.The interface that lies at the gate oxide and electrolyte soution various chemical reactions take place,the default formulation of well known site binding model has been executed. The impact of pH on the threshold voltage shows shift of 58.1, 60.6, 61, 61.5 and 57.6mV/H for various oxide layers of Sio2, Si3N4, Al2O3, Ta2O5 and Hfo2 respectiively.The device shows a maximum sensitivity of 59.9, 60.6, 63.4, 61.5 and 60.3 mV/pH for the above mentioned oxides.

III. METHODOLOGY

In our thesis,we have investigated an underlap structure of dual gate organic field effect transistor (DGOFET) containing electrolyte/watery solution is explored to improve the Nernst limit (59mv/pH) of sensitivity. After incorporating the electrolyte medium in DG-OFET,effect of pH change on device characteristics for instance drain current vs gate voltage,voltage sensitivity and current sensitivity are examined.The charge density at the interface of oxidesilicon interface of OFET is obtainesd as a function of electrolyte pH from physics based modelling. The proposed methodology will be done by using SILVACO ATLAS. The main objective of this work is to build a a dual gate organic field effect transistor (DG-OFET) based pH sensor that will be able to detect the variations in the aqueous (electrolyte) medium .In this structure source sided underlap technique with dual gate sensing approach has been used. The simulated results display that the proposed DG-OFET shows significantly higher sensitivity for different dielectrics. The voltage sensitivity achieved by DG-OFET in our work is 217.53 mv/ph which surpasses the Nernst Limit nearly 4 times.

IV. DEVICE STRUCTURE AND OPERATION

For calculation of acidity and alkalinity i.e, the approach of pH was earlier recomended by S. P. L. Sørensen in1909.[5] This was followed by Beckmann's prominent device for checking acidity[3] and a fine glass diaphragm based electrode for differential measurement[4]. Numerous techniques have been reported to enable pH detection which includes optical fiber,mass-cantilever devices,metal oxide transistors,conducting polymers,nanostructured cantilever,or even pH color matrix. A major achievement for sensing in chemical and biological applications has been achieved by inorgnic semiconductors with the inaugration of ion-sensitive field effect transistors (ISFETs) in 1970 [1] [2]. With the prime objective of developing a transducer that will be low cost,disposable and can be used for various biochemical applications,we have realized an organic sensor that will be able to measures the phenomena that occur at the electrolyte/dielectric interface of the organic semiconductor by the field enhanced conductivity.On the basis of this sensing principle, a convenient detection layer is added to the transistor in order to upgraded selectivity of transistor and to provide particularity towards ion or neutral molecules and biomolecules.The detection technique resembles with the silicon based field effect chemical sensor,in such a manner that deviation in pH causes the adjustment in the voltage drop across the dielectric/semiconductor interface thereby causing current variations[3].

In living organism the biochemical significance of pH lies in the blood, where even a minute change of about 0.05 pH units have a intense effect on the operation of the human body. Aside from gastric fluids which shows very acidic pH levels (pH about 2), the bodily fluids containing blood, urine, saliva, tears, and sweat, shows a standard range from pH 5 to 8. pH has biochemical significance in living organism especially in blood where a change of even 0.05 pH units have a profound effect on the functioning of the human body [3], specific values for body fluids including blood, urine, saliva, tears and sweat range from ph 5 to 8.

V. PROPOSED DEVICE SIMULATED STRUCTURE

The simulation of our device is implemented using ATLAS (Silvaco) TCAD tool. In order to sense the pH of electrolyte using Pentacene based DG-OFET the proposed structure consist of Aluminium layer of thickness 30nm used as gate electrode.

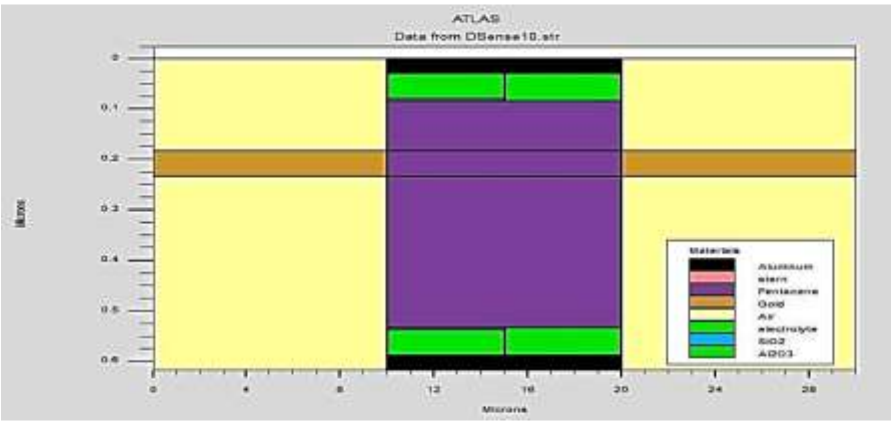


Figure 1: Proposed Device Structure of DG-OFET based pH sensor

On top of which lies electrolyte of thickness 50nm, which is then followed by stern and oxide layer of thickness 1nm and 3nm as mentioned in Table 1 respectively. On top of this oxide layer a 400nm thick organic semiconducting layer of pentacene is deposited and 50nm thick patterened source and drain electrodes of gold were defined. As in this proposed structure we are sensing pH of an electrolyte on both side so the pentacene layer is again followed by oxide,stern and electrolye respectively as shown in given Figure 1.The calibration is done according to the work.

Table 1: Proposed Device Dimensions

Parameter Name	Parameter Value
Channel length Channel Width Oxide Thickness	30 nm 1 µm 3 nm

A. *Device Operation*

To observe an underlap DG-OFET device that is sensitive to the pH of the electrolyte in which equal amount of positive (cation) and negative ion (anion) in aqueous environment can be modelled as intrinsic semiconductor having zero energy band gap and permittivity of water [9]. The similarity between Poisson- Boltzmann equation for ions of electrolyte and electrons-holes pairs in intrinsic semiconductor is used for the modelling of electrolyte as a semiconductor in the simulation [7]-[8]. Various parameters used has been given.

Table 2: List of setup parameters for pH sensor design in ATLAS Simulator

Material	Parameter	Value
Pentacene(Organic Semiconductor)	Ionization Potential	5.2 eV
	Electron Affinity	2.8 eV
	Dielectric Constant	4
	Hole Mobility	0.85cm2/vs
	Band gap energy at 300K	2.2 eV
Gold(source/drain)	Work function	5.1 eV
Gate(Aluminium)	Work function	4.08 eV

Table 3: Value of parameters for Sio2 and Al2O3

Symbol	Sio_2	Al_2o_3
Er $N_s(cm^{-2})$ KaKb Band gap(eV)	3.9 5×10^{14} 10^{-6} 10^{2} 9	14 8×1014 10-10 10^{-6} 8.8

VI. RESULTS

The simplified geometry of DG-OFET described in Fig. 1 is a combination of DG (top gate) stacked on a BG(bottom gate) OFET; the two devices share the source and drain electrodes and the organic layer.In our case, the DG-OFET structure is asymmetric due to difference between the organic layer thicknesss in top and bottom gate OFET structure.In our design the primary gate is the top gate and the bottom gate will be reffered to as secondary gate.

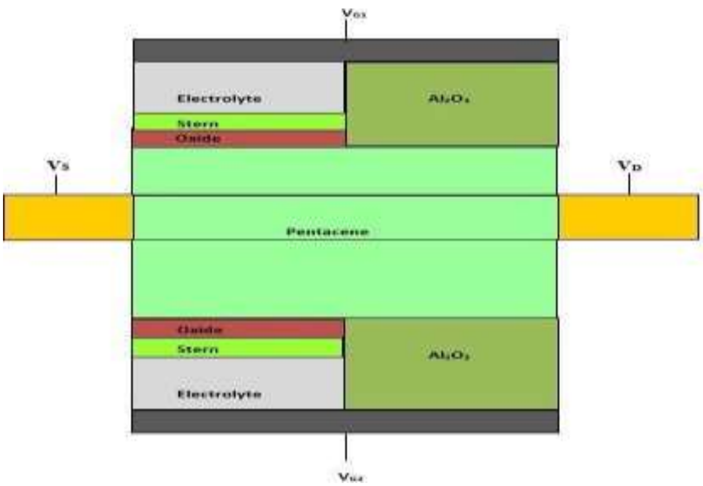


Figure 2: Device structure of DG-OFET based pH sensor

VII. DEVICE CHARACTERISTICS

The performance of our proposed pentacene based DG-OFET were measured to understand the basic operations and characteristics of the device. It is observed from the simulated device characteristics that our device shows typical P-type transistor behavior and is typically shown in both Drain and Transfer characteristics in Fig 3(a) and Fig 3(b).

A. Drain characteristics

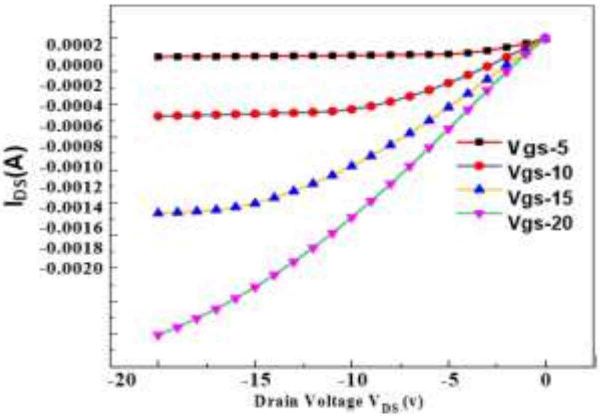


Figure 3: (a) The drain characteristics of DG-OFET measured at gate voltages Vgs= -5 V,-10V, -15V, and -20 V when Vds is sweeped from 0 to 20 V with step size of 1 V.

B. Transfer characteristics

The transfer characteristics of the devices at various gate biasing has been shown in Figure 3 (b)

(b)

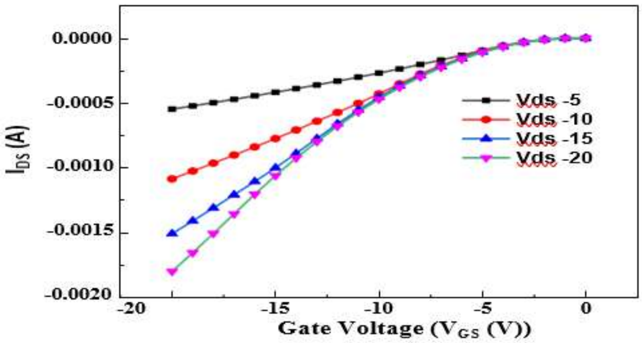


Figure 3: (b) The transfer characteristics of DG-OFET (b)in linear scale Vds= -5 V,-10V, -15V, and -20 V when Vgs is sweeped from 0 to -20 V with step size of 1 V

C. 4pH Sensing Performance For Sio2 As Oxide

Channel material is kept pentacene for these simulations, whereas the oxide will be changed with Sio2, Hfo2 and Ta2o5 respectively. The shift in drain current is towards right as value of the pH increases. The choice of oxide may help in many ways from high sensitivity to longer device life time. The electrolyte can be acidic or basic so its contact might imitate device working and may damage the oxide which in turn will affect the site binding charge and consequently affect the performance of the device.The choice of oxide may also influence in terms of power consumption.. The choice must be based on whether we want more sensitivity or more energy saving.With SiO2 as oxide, drain current versus gate bias voltage is drawn as shown in Figure 4. SiO2 has long been used as an oxide for its easy availability.Change is observed in the form of threshold voltage. Simulation has been performed at Vds=-3 V and Vgs=-8 V and results have been plotted in logarithmic y-axis. Results show promising values better shift than previous results discussed in literature review.

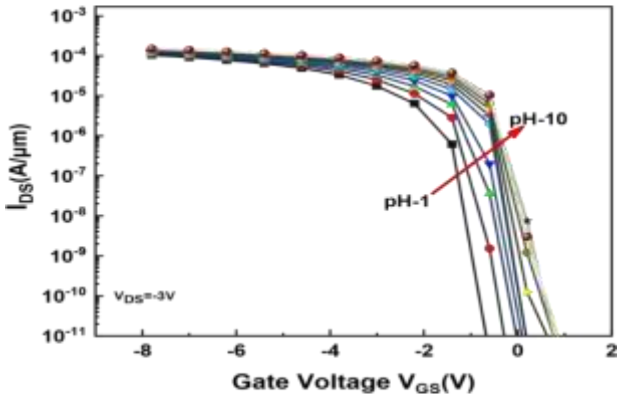
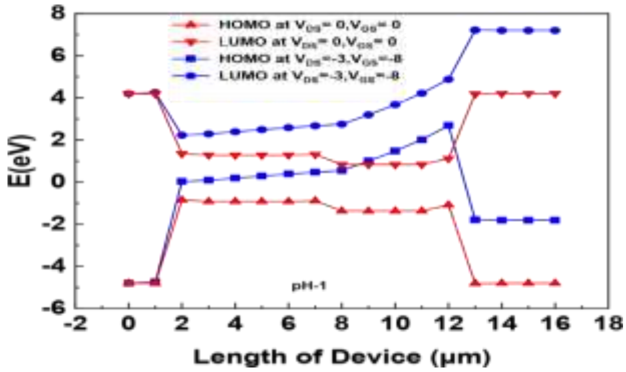


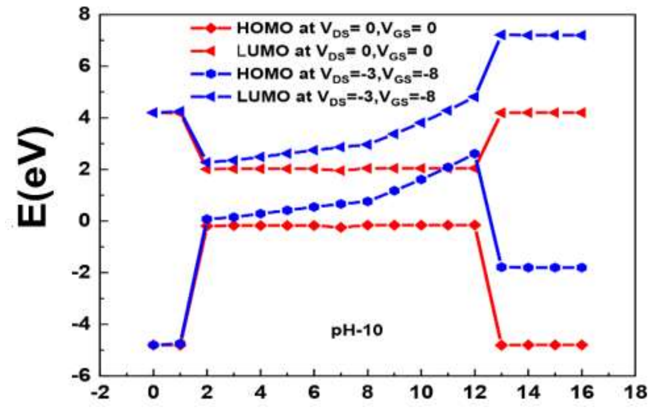
Figure 4: Drain current (Ids) vs gate voltage (Vg) as a function of pH varying from 1 to 10

D. 4 Variation of Energy Bands

The variation of energy band for DG-OFET is shown in the Figure 5 (a) and (b).



(a)



(b)

Figure 5: (a) and (b) showing band bending in valance band and conduction band under bais and no bias condition for ph=1 and ph=10 respectively

A cutline is made at 1nm below the oxide-channel interface atVgs = 0V,Vds = 0Vand Vgs=-8V, Vds = -3V and the energy levels of HOMO and LUMO are extracted. Figure 6 shows the variation of HOMO and LUMO for pH values of 1, 5 and 10 for DG-OFET respectively. When pH is changed by causing change in surface potential thereby causing an increase in current density,which in turns results in band bending.From the above graph its clear that with increase in pH,band bending increases.

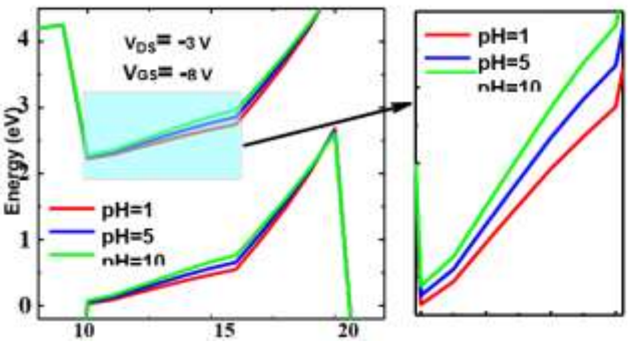


Figure 6: variation of energy band for three value of ph=1,5 and 10 for DG-OFET based pH Sensor

E. Electric Field And Potential

Figure 7 (a) and 7(b) shows the plot of electric field distribution and potential along the length of channel of the proposed device .The plot has been drawn by taking a cutline at 1nm below oxide semiconductor interface at VGS=8v and VDS=-3 V respectively. With change in pH from 1 to 10 it has been observed that potential decreases whereas electric field increases.The high electric field is achieved at pH=10 whereas potential is at its lowest at pH=1.

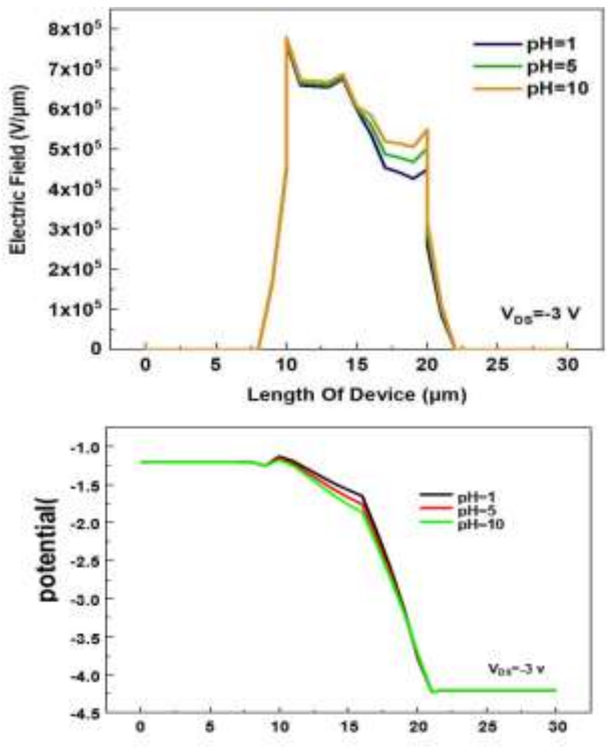


Figure 7: shows Electric Field along the device length (b) shows potential along the device length forpH=1,5 and 10 at VGS=8 V and VDS=-3 V respectively

F. Voltage Sensitivity And Current Sensitivity

The utmost significant factors to estimate the sensing ability of a biosensor or ISFET is voltage sensitivity (SV) and current sensitivity (SI). Traditionally in FET-based biosensors the sensitivity of the device is calculated as a alteration in threshold voltage or ratio of change of drain current at a particular gate voltage. Voltage sensitivity (SV) is calculated for a constant value of drain current (IREF). For a specific value of drain current (IREF) the corresponding responsive gate voltage (VR) is obtained and the shift in that gate voltage (ΔVR) with respect to a pH value can be used to find voltage sensitivity (SV). In our work we have calculated ΔVR for a specific value of IREF as ΔVR (at any pH) = VR (at any pH) - VR (at pH=1). In Figure 8 the curve of ΔVR vs pH for reference values of drain current (IREF) = 10-6 A, 10-7 A, and 10-8A, is shown. The voltage sensitivity (SV) attained by DG-OFET device for IREF values of 10-6 A, 10-7 A, and 10-8A are 217.53 mV/pH, 146.26 mV/pH, and 142.99 mV/pH respectively .Thus the voltage sensitivity achieved by DGOFET in this work is 217.53 mV/pH which surpasses the Nernst limits by more than 3.6 times.

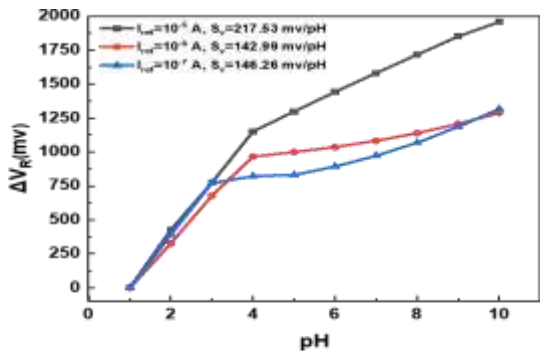


Figure 8: Variation of responsive gate voltage (ΔV_R) with pH for drain current of (I_{REF}) of 10^{-6} A, 10^{-7}A,10^{-8}

G. *Current Sensitivity*

The drain current sensitivity (SDRAIN) represents ratio of change of drain current as a function of VGS. So the drain current sensitivity is calculated as Sdrain = [Idrain (at any pH) -I0/ I0] where I0 is the drain current obtained at pH=1. Figure 9 shows the current sensitivity of DG-OFET devices and it can be seen that the maximum sensitivity achieved by the devices is nearly greater than 106 for pH =10 while taking current at pH=1 as reference . From the graph it is clear that there is significant increase in the sensitivity of the proposed device.

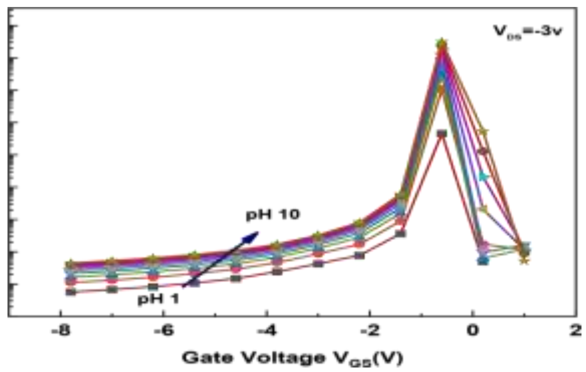


Figure 9: Drain current sensitivity as a function of VGS at different pH values ranging from 1 to 10

H. ON-OFF Current Ratio

Figure 10 shows the variation of on-off current ratio with resect to the different pH values. The on/off current ratio which is defined as the ratio of accumulation (on-state) to depletion(offstate) and performance of any transistor intensely depends on the sameratio.The thickness of the semiconductor and dielectric,channel conductivity,charge density,mobility actually influences this current ratio.Moreover, high dielectric constant of the insulator and a high gate capacitance impacts the higher value on/off.Overall,the Ion/Ioff greater than 106 is desired.A low Ioff is essential for low power consumption applications.So it is evident from the graph that with increase in pH value of the device the ON-OFF current ratio decreases and the Ion/Ioff is greater than 106.

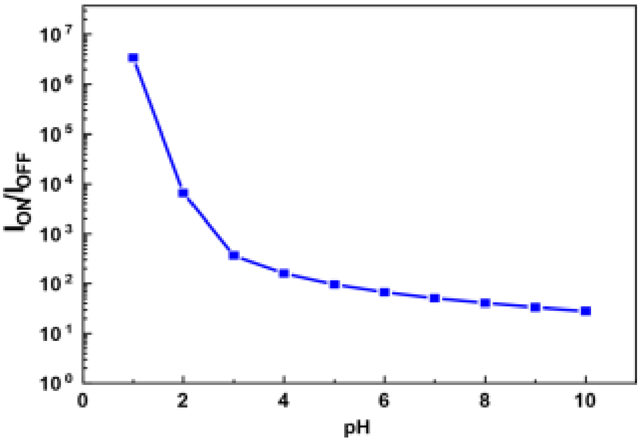


Figure 10: ON-OFF current ratio with respect to pH values at Vds=-3 V

VIII. OBJECTIVES

The main objective of this work is to build a a dual gate organic field effect transistor (DG-OFET) based pH sensor that will be able to detect the variations in the aqueous (electrolyte) medium .In this structure source sided underlap technique with dual gate sensing approach has been used. The simulated results display that the proposed DG-OFET shows significantly higher sensitivity for different dielectrics. The voltage sensitivity achieved by DG-OFET in our work is 217.53 mv/ph which surpasses the Nernst Limit nearly 4 times. pH recognition with high resolution has gained enormous research attention over the past decade and such sensors are needed to detect malignant tumors and other diseases in human blood. In this work detailed study of dual gate organic field effect transistor device having source sided underlapped region which is sensitive to aqueous electrolyte environment is done ,the results shows that the DG-OFET based device can be preferred for the use of pH sensing applications. Proposed device had a sensitivity of 217.53 mV with SiO2 as gate oxide which is nearly 4 times of Nernstian limit.The organic transistors have shown outstanding enhancement,but in order to make organic devices practically viable many challenges still need to be resolved.The device structure, device dimensions and material used for different layers, determine the performance of these organic transistors.Future work involves the formation of a schottky contact at the interface between the active layer and gate that shows high performance due to use of vertical channel structure.Further,cylindrical gate(CG) OTFTs have aslo turned out to be promising and can be tried.Moreover cylindrical structures are intended for size reduction,thereby aiming for higher packing density.Apart from this we can make use of different organic materials such as P3HT,tetracene,anthracene,PCBM, PTAA, PVTT, PVP, PVA, PMMA,P4VP, P4DDT and many nano-micro-sized altered synthesized organic materials to enhance the performance of our device.

IX. DISCUSSION

With the advent of the Internet of Things (IoT) era, flexible sensors are regarded as one of the most important technologies for the development of human friendly wearable devices. Organic field-effect transistors (OFETs) based on conjugated polymers or small molecules are promising sensor platforms because they have various advantages, including high sensitivity, mechanica flexibility, and low-cost fabrication processes. OFET-based sensors enable continuous monitoring of external stimuli or target analytes with superior detection capabilities. To observe the changes in the concentration of hydrogen ion in an aqueous solution Ph sensors can be used.Modelling of the electrolyte region has been done with the equal amount of positive(cation) and negative(anion) ion in aqueous environment which can represent the intrinsic semiconductor ions .Thus numerous changes that occur on threshold voltage, potential, drain current and sensitivity due to pH changes can be encountered.So variations in the threshold voltage of the device may be described as the pH response while the pH is varied.The current characteristics shows variation when pH is changed from acidic to basic.Various other effects that came into play such as thickness of oxide and device dimensions has also been studied. Hence our work has mainly focussed on improvement of sensitivity which is based on change in threshold voltage. Work has been done to increase sensitivity up to 217.53mV.The dimensions of the device can also serve as an important parameter to improve the performance. Therefore, in order to get the maximum probable results device should be designed with optimum dimensions

X. CONCLUSION

pH recognition with high resolution has gained enormous research attention over the past decade and such sensors are needed to detect malignant tumors and other diseases in human blood. In this work detailed study of dual gate organic field effect transistor device having source sided underlapped region which is sensitive to aqueous electrolyte environment is done ,the results shows that the DG-OFET based device can be preferred for the use of pH sensing applications. Proposed device had a sensitivity of 217.53 mV with SiO2 as gate oxide which is nearly 4 times of Nernstian limit.

The organic transistors have shown outstanding enhancement,but in order to make organic devices practically viable many challenges still need to be resolved.The device structure, device dimensions and material used for different layers, determine the performance of these organic transistors.Future work involves the formation of a schottky contact at the interface between the active layer and gate that shows high performance due to use of vertical channel structure.Further,cylindrical gate(CG) OTFTs have aslo turned out to be promising and can be tried.Moreover cylindrical structures are intended for size reduction,thereby aiming for higher packing density.Apart from this we can make use of different organic materials such as P3HT,tetracene,anthracene,PCBM, PTAA, PVTT, PVP, PVA, PMMA,P4VP, P4DDT and many nano-micro-sized altered synthesized organic materials to enhance the performance of our device.

VIII. FUTURE SCOPE

Future work involves the formation of a schottky contact at the interface between the active layer and gate that shows high performance due to use of vertical channel structure.Further,cylindrical gate(CG) OTFTs have aslo turned out to be promising and can be tried.Moreover cylindrical structures are intended for size reduction,thereby aiming for higher packing density.Apart from this we can make use of different organic materials such as P3HT,tetracene,anthracene,PCBM, PTAA, PVTT, PVP, PVA, PMMA,P4VP, P4DDT and many nano-micro-sized altered synthesized organic materials to enhance the performance of our device.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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