CHAPTER-3

Low-voltage TFT based Efficient Ammonia Sensor with Controlled Morphology of Sensing Film over LaZrOx high-k Dielectric Film

The part of the work is adopted from-

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Abstract:

In this chapter, a self-aligned, cost-efficient, fully solution-processed, low voltage operated high-k dielectric-based p-channel organic thin film transistor (OTFT) has been developed and investigated for toxic ammonia analyte at RT (room temperature – 25 ºC). A spin casting method has been utilized to deposit a high-k dielectric, LaZrOx, on a p++ silicon substrate. The organic semiconductor channel deposition uses minimal wastage self-assembly floating film transfer method for P3HT growth over HMDS treated LaZrOx dielectric. The doping of lanthanum in ZrOx material reduces the charge traps and RMS surface roughness and also minimizes the other surface defects and carrier scattering at the dielectric interface. The solution-processed dielectric material is suitable for low voltage operated OTFT due to its high capacitance per unit area of 486 nF/cm^2 at 1 kHz and a low leakage current density of ~0.5×10^{-8} A/cm^2 at -2 V. Even at a low operating voltage of -2 V, the fabricated OTFT is capable of producing a good saturated current. The OTFT sensor results in a high response of 47% at 5 ppm NH_3 analyte and a low detection limit of 11.65 ppb. The developed sensor exhibits a low average response, recovery time of 9 sec. and 50 sec., and is almost independent of relative humidity variations in the range of 30% to 70%. The study reveals that this novel low-voltage OTFT device is capable of operating at -2 V and has shown a high sensitivity towards ammonia gas detection at RT.

3.1 Introduction

Over the last few decades, the scientific community has shown considerable interest in solution-processed TFT (thin-film transistors) and self-powered devices because of their potential applications in sensors, actuators, displays, numerous electronic circuits, etc. [60], [157],

[158]. The OTFT offers multi-parameter characteristics to characterize the device performance in various real-time applications in terms of threshold voltage, subthreshold swing, mobility, etc. [65]. Although the conventional SiO_2-based OTFT has a potential advantage in terms of defect-free oxide film, compatibility with CMOS technology, high thermal conductivity, etc., it requires a very high operating voltage (>20 V) [42]. The conventional SiO_2-based OTFT suffers from low dielectric constant (k – 3.9), high tunneling current at low oxide thickness, high static, and dynamic power dissipation due to large V_{DS} in comparison with high-k dielectric materials (ZrO_2, HfO_2, Ta_2O_5, etc.) based OTFT. The tradeoffs of conventional SiO_2 have been countered by utilizing an appropriate high-k dielectric film as a gate oxide. The dielectric film with a high-k value offer high capacitance, high current value, low threshold potential (V_{TH}), and minimize the effect of tunneling current at low oxide thickness [159].

Several researchers have already reported the effect of high-k dielectrics as a gate oxide, such as $LiZnO_2$ [160], HfO_2 [161], ZrO_2 [162], etc. These dielectrics have been used with inorganic/organic materials as a semiconductive channel to fabricate a TFT. The use of novel metals, such as lithium, lanthanum, etc., in the metal oxide improves the dielectric constant, dielectric properties, and drive current of the transistor [163][164]. It is imperative to optimize the solution-processed dielectric film's morphology, microstructure, dielectric film thickness, root mean square surface roughness ($\sigma_{rms} < 1$ nm), and uniformity for optimum performance of solution-processed OTFT [159][165]. A smooth dielectric surface offers nanoscopic oriented grains, a superior dielectric semiconductor interface with a suppressed charge scattering and charge trapping, and enhances the charge transport phenomenon [165].

Therefore, the fully solution-processed low voltage inorganic dielectric-based OTFT is somewhat challenging to fabricate but, once achieved, has numerous potential uses in the field of electronic circuits and sensors.

The present work uses lanthanum zirconium oxide (LaZrOx) (k =22) composite as a dielectric layer for solution-processed, low-voltage operated TFT device for NH_3 sensing. The developed dielectric exhibits a low dielectric surface roughness of (0.534 nm), high dielectric constant (k = 22), smooth uniform thin layer, low leakage current, and a prominent response towards ammonia analyte at room temperature (RT). The zirconium oxide (ZrO_2) with a Gibbs energy ΔG of −47.1 kJ/mol (0 to -50 KJ/mol is favorable for oxide material), causing it almost free from moisture absorption, which makes the doped ZrO_2 a very stable material even in normal ambient conditions [165]. The current work includes a solution-processed OTFT device for ammonia sensing. In recent years ammonia sensing has gained more interest among researchers due to its prominent application in the fertilizer industry, cooling plants, water purification plants, and many more applications [108]. The long time exposure (OSHA limit 35 ppm for 15 minutes [166]) of this highly toxic, suffocating odor, colorless, highly irritating gas cause severe and fatal effects on flora and fauna [167][168]. Hence, the fabrication of a reliable and high responsive ammonia sensor is very important to avoid causalities and life-threatening situations. The present work has developed a novel low voltage solution-processed top contact bottom gate (TCBG) TFT-based ammonia sensor using a cheap FTM (floating film transfer) method. The work aims to develop a cost-effective, simple, low-power consumption solution-casted organic TFT device for ammonia sensing application at room temperature (RT- 25 ºC).

3.2 Experimental Procedure

3.2.1. Materials and Methods

P3HT (Poly(3-hexylthiophene-2,5-diyl)) (Regioregularity-97.6%) (MW- 27k to 45k) was purchased from Ossila ltd. U.K. chloroform ($CHCl_3$), TCE (Trichloroethylene), Isopropyl alcohol (IPA), Hydrogen peroxide (H_2O_2), Sulfuric acid (H_2SO_4), HMDS (Hexamethyldisilazane), Zirconium (IV) acetylacetonate, Lanthanum acetate hydrate, Glycerol, Ethylene glycol, Methanol and 2 ME (2 Methoxy Ethanol) was purchased from Merck India Pvt. Ltd. All the processing chemicals have been used as it is without any purifications.

A 100 mM solution of Zirconium (IV) acetylacetonate ($Zr(C_5H_7O_2)4$) (ZrAc) and 300 mM of Lanthanum acetate hydrate ($La(CH_3CO_2)_3 \cdot xH_2O$) (LaAc) was dissolved separately in 2 ME and, was stirred at 900 rpm for 6 hours at 50 ºC to form a clear solution. In the subsequent step, a dielectric/gate oxide solution was prepared by mixing 6:1 of previously prepared ZrAc and LaAc in a separate vial tube. The mixed solution was agitated at 900 rpm for 3 hours at 50 ºC to obtain a uniform homogenous solution and filtered by a 0.22 µm pore size PTFE syringe filter to eliminate heavy particles. For the OSC (organic semiconductor channel), 6 mg of P3HT was dissolved in $CHCl_3$ and stirred for 1 hour at RT.

3.2.2. Device Fabrication

The following steps have been adopted to fabricate this device. The p++ Si substrate was cleaned ultrasonically with TCE, then propanol, and rinsed with running DI water. Further, the substrate was dipped in piranha solution (H_2O_2: $H_2SO_4 = 6:4$) for 15 minutes and rinsed with running DI water. The native oxide layer was then removed by HF treatment for 2 minutes, followed by rinsing with running DI water. The surface activation was carried out by oxygen plasma treatment for 10 minutes to eliminate the -OH- (hydroxyl) groups from the cleaned wafer. The plasma cure helps to form an adhesive defect-free cleaned Si substrate. The prepared dielectric or gate oxide solution was spin-casted at 4500 rpm for 50 sec. to obtain a uniform spin-casted film. Further, the obtained film was baked at 80 °C, followed by annealing at 625 °C for 60 minutes in nitrogen ambient to form a 40±3 nm (indicated in cross-sectional SEM **Figure 3.4 (a)**) uniform thickness oxide film. The fabricated dielectric film was further processed with the Hexamethyldisilazane (HMDS) vapor phase technique to form a hydrophobic surface or self-assembled monolayer by controlling the processing time and temperature [169]. After that, a 25±4 nm OSC (measured by Filmetrics F20-UV)) is deposited using the FTM on HMDS-treated p++/ $LaZrO_x$ and annealed at 80 °C for one hour to eliminate the residues of organic solvent. The basic steps of the floating film transfer method are shown in **Figure 1.5**.

A 50 nm gold drain/source interdigitated pattern with a channel width of 18 mm and length of 50 μm was deposited on FTM deposited polymer film by thermal evaporation unit HHV 12A4D at a ~10^{-6} torr pressure using a nickel shadow mask. **Figure 3.1(a)** and **Figure 3.1(b)** show the OEFT device schematic and fabricated device image, respectively.

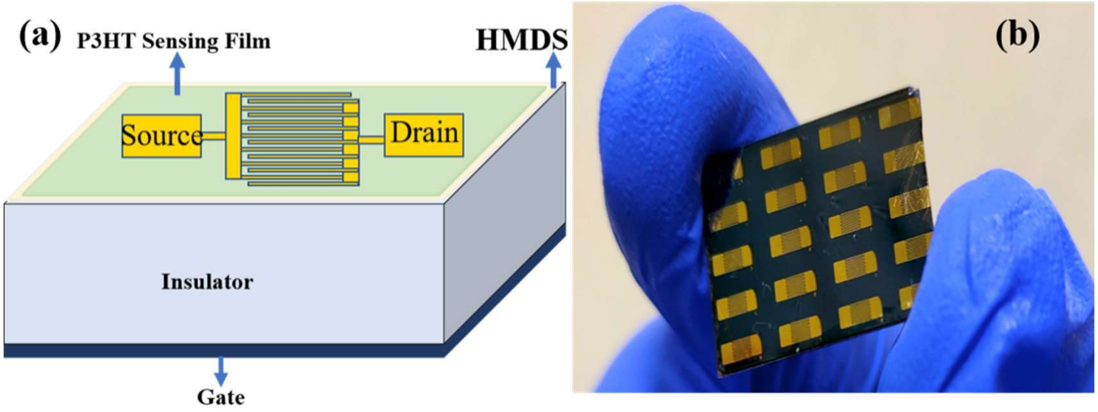

Figure 3.1(a) OTFT device schematic, (b) Fabricated device image.

3.3 OTFT Characterization and Sensing Setup

The XRD (X-Ray diffraction) plot of the fabricated dielectric and P3HT film using "Rigaku smart lab 9 KW" equipped with a Cu Kα source is shown in **Figure 3.2(a)**. At 29.50º, the LaZrOx exhibits a strong peak (111), followed by (200), (220), and (331) at 34.64º, 49.75º, and 59.6º, respectively [170]. The P3HT polymer has a strong peak (100) at 5.96 degree, as well as higher-order peaks (200) and (300) at 11.30 degrees and 16.64 degrees, respectively [16]. The XRD pattern of the P3HT shown in **Figure 3.2(a)** with sharp peaks confirms the crystalline and highly oriented nature of the polymer film. The improved crystallinity and chain ordering of the polymer film are due to the self-assembly nature of the FTM-deposited OSC film. The mixture of LaAc solution and ZrAc solution improves the dielectric material's quality in terms of RMS surface roughness, dielectric band gap, etc. [170]. The tauc plot of the synthesized LaZrOx gate oxide is illustrated in **Figure 3.2(b)**. The fabricated dielectric has a band gap of 5.25 eV, which is quite enough for the gate oxide of the OTFT device.

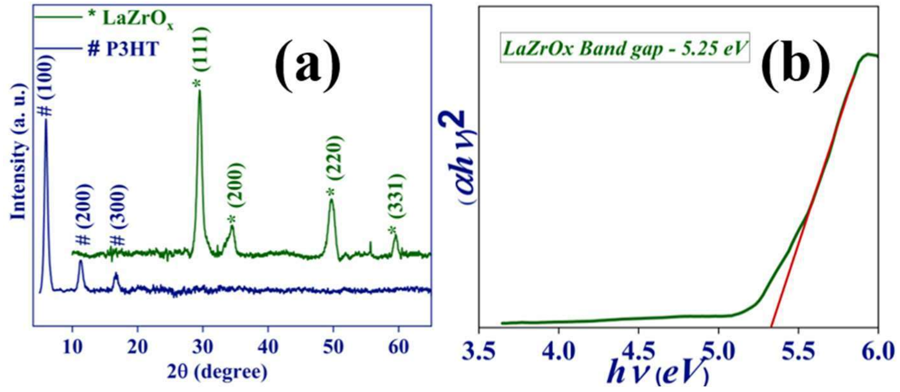

Figure 3.2 (a) XRD pattern of LaZrOx dielectric and P3HT film, (b) Tauc's plot of fabricated LaZrOx dielectric film.

AFM (Atopic force microscopy) (Model - NTEGRA Prima- NT-MDT) and SEM (Scanning Electron Microscopy) (Company- CARL ZEISS MICROSCOPY, Model - EVO - SEM

MA15/18) has been used to investigate the surface topology of the synthesized solution-processed dielectric film and FTM deposited P3HT polymer film. The fabricated LaZrOx dielectric film has a very low RMS surface roughness of 0.534 nm (indicated in AFM results in **Figure 3.3(a)** 2D and **Figure 3.3(a')** 3D images), while the bare ZrO_x offers comparatively higher roughness of 0.909 nm (indicated in **Figure 3.3(b)/(b')**). The low RMS roughness is advantageous for OTFT manufacturing as it reduces carrier scattering [165]. In the present work, the ratio of ZrAc and LaAc has been optimized to obtain a high dielectric constant (k-22), high bandgap, and smooth surface. The variation in dielectric constant with different ratio of ZrAc and LaAc in **Figure 3.4(c)** illustrate that 6:1 is the optimized ratio with dielectric constant 22. The AFM image of the fabricated $LaZrO_x$ dielectric film with optimized solution exhibits low RMS surface roughness of 0.534 nm at 6:1 ratio of ZrAc, and LaAc is shown in **Figure 3.3(a)/(a')**. The average surface roughness of the FTM deposited P3HT active layer is 4.2 nm, shown in **Figure 3.3(c)/(c')**, which provides large gas adsorption/desorption reactive sites, and incorporates into the gas sensing phenomenon of the sensor [171].

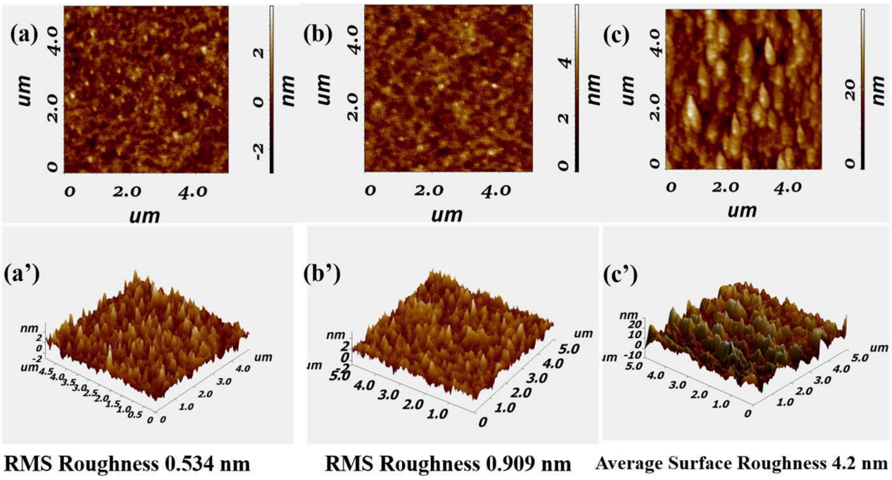

Figure 3.3 (a) & (a') 2D, 3D Tapping mode AFM image of LaZrOx dielectric, (b) & (b') 2D, 3D AFM image of bare ZrOx film under tapping mode, (c) & (c') 2D, 3D AFM image of pristine P3HT film under tapping mode.

The cross-sectional SEM picture of the dielectric film and SEM image of P3HT film over gate oxide film is shown in **Figure 3.4(a)** and **Figure 3.4(b)** (Inset plot), respectively. The cross-sectional SEM shows a solution-processed dielectric film of ~40 nm has been deposited over a p^{++} silicon substrate. The SEM picture of the P3HT polymer film (inset **Figure 3.4(b)**) shows a smooth and uniform film morphology has been obtained using the FTM method.

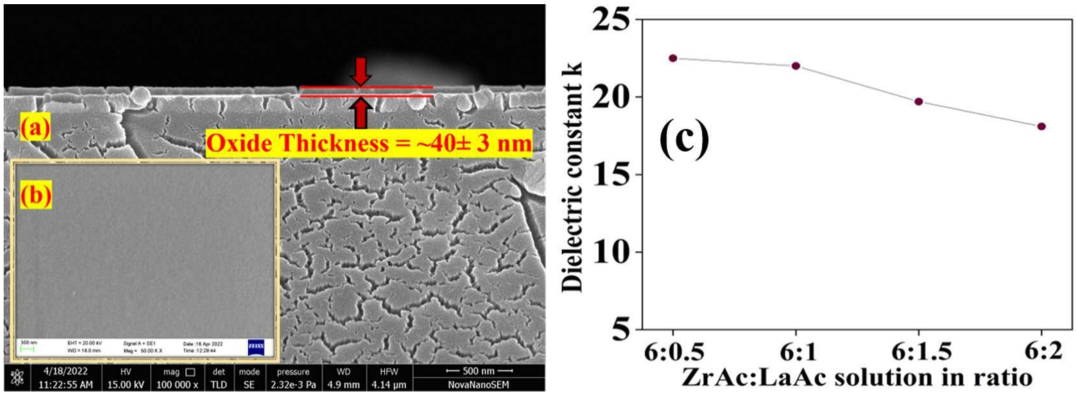

Figure 3.4 (a) Cross-sectional FESEM image of developed LaZrOx dielectric on p++ silicon substrate (dielectric thickness = ~40±3 nm), (b) SEM image of pristine P3HT polymer over p++ (Si)/LaZrOx/HMDS substrate, (c) Dielectric constant (k) with different ZrAc: LaAc ratio.

In the present work, a customized sensing setup with a temperature controller, humidity sensor, inlet valve, outlet valve, mixing fan, etc., has been deliberately utilized for ammonia sensing. The mass flow controller has been used for the gas inlet with precise concentration at a 10 ml/minute flow rate from an ammonia sample diluted by dry N_2 gas for low-concentration testing. **Figure 3.5** shows a schematic of the customized gas sensing setup. The ambient atmospheric condition has been maintained with RT = ~25 ºC and 54% relative humidity (RH) throughout the all-sensing characterization; however, the section "**Influence of Relative Humidity on NH3 sensing**" has been performed to investigate the effect of RH on the sensing response of the sensor at 5 ppm NH_3 gas. The electrical characterization has been done with the help of the semiconductor parameter analyzer KEYSIGHT B1500A for various measurements.

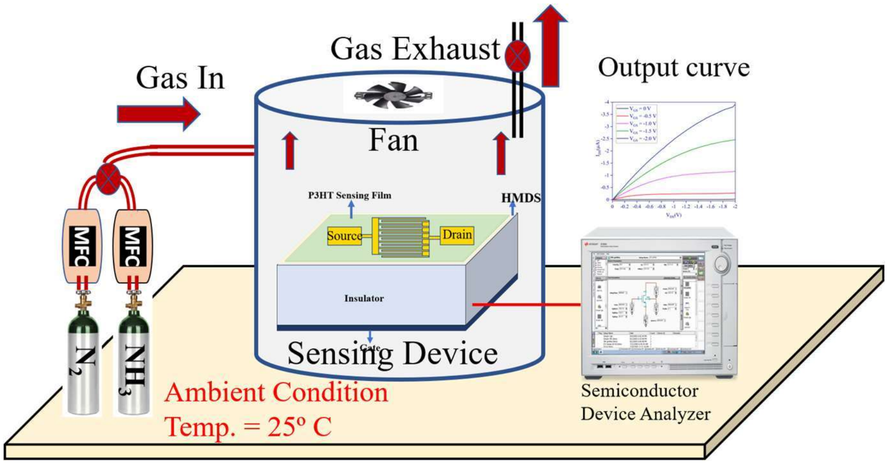

Figure 3.5 Schematic of indigenous sensing setup.

3.4 Electrical and Sensing Characterization

3.4.1. Electrical Parameters of the Fabricated OTFT

The operating voltage of the fabricated OTFT depends upon the nature of gate oxide material, OSC material, and thickness of dielectric and OSC film. The current work has optimized the electrical and sensing characterization of the fabricated OTFT for an operating voltage of $V_{GS} = V_{DS} = -2$ V.

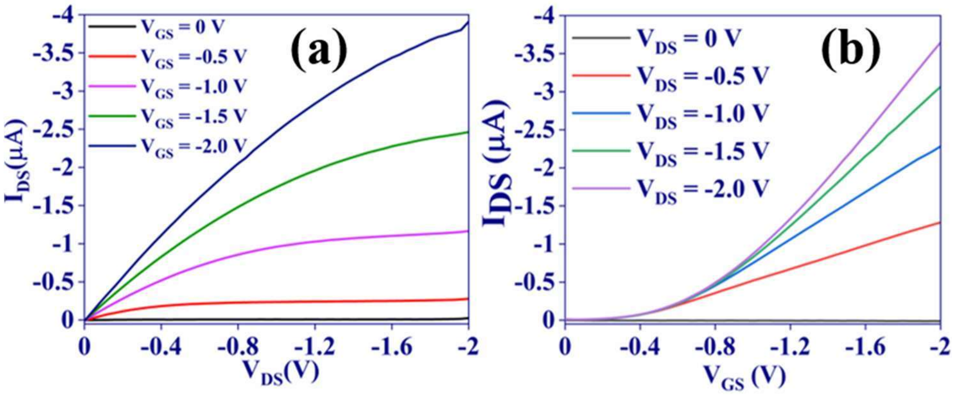

Figure 3.6 (a) I_{DS} vs. V_{DS} characteristics of fabricated OTFT device, (b) I_{DS} vs. V_{GS} characteristics of the fabricated low voltage operated OTFT device.

Figure 3.6(a) and **Figure 3.6(b)** show the I_{DS}-V_{DS} (Drain characteristics) and I_{DS}-V_{GS} (Transfer characteristics) plots for the fabricated device, respectively. At $V_{GS} = V_{DS} = -2$ V, the device has a saturated current of -3.9 μA, indicating that the solution-processed OTFT is suitable for use with a -2 V operating voltage. **Figure 3.6(b)** shows the I_{DS}-V_{GS} plot of the fabricated device for 0 to -2 V_{GS} sweep at 0.5 V drain step voltage.

The solution-processed high-k $LaZrO_x$ has an advantage in terms of low leakage density, the wide band gap of 5.25 eV. (reduces leakage current), and high capacitance of ~486 nF/cm^2 at 1 kHz frequency. The high capacitance per unit area of the dielectric film offers a high charge density at a lower voltage, resulting in a low voltage operation of the transistor. **Figure 3.7(a)** and **Figure 3.7(b)** show the capacitance vs. voltage plot (C-V plot) and leakage current density plot for fabricated LaZrOx dielectrics film, respectively. The leakage current density plot confirms that the device remains in satisfactory operation up to an operating potential of -5 V. This ensures that the LaZrOx dielectric exhibits very low pinholes in the gate oxide film, which is necessary for high-performance OTFT. The dielectric film's high capacitance/area has the ability to improve the transistor's current carrying capability at an extremely low leakage current density of ~0.5×10^{-8} A/cm^2 at -2 V.

The drain current (I_{DS}) of the fabricated OTFT in the saturation regime has been expressed by Equation **(3.1)** [16]

$$I_{DS} = \mu_P C_d \frac{W}{2L}(V_{GS} - V_{TH})^2\ ;\ V_{DS} \geq V_{GS} - V_{TH} \tag{3.1}$$

Where μ_P, V_{TH}, W/L, V_{DS}, and V_{GS} represent mobility, threshold voltage, aspect ratio (AR), drain-to-source potential, and drain-to-gate potential of the device, respectively. C_d denotes the capacitance per unit area of the gate oxide film.

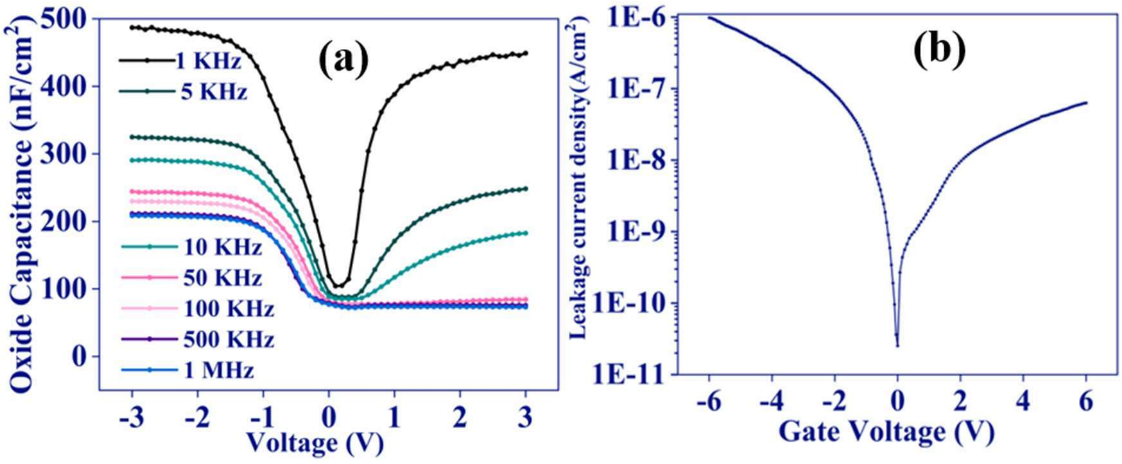

Figure 3.7 (a) Oxide capacitance vs. gate voltage plot of LaZrOx dielectric at various frequency (1 kHz – 1 MHz), (b) Leakage current density vs. gate voltage plot of the fabricated dielectric.

The parameters mobility (μ_P) and threshold voltage (V_{TH}) of the fabricated OTFT device are obtained graphically from the linear fit of $\sqrt{I_{DS}}$. A detailed discussion about μ_P, V_{TH} extraction is given in the article - [17], and equation (3.2) can be used to extract the subthreshold swing of the transistor [172].

$$SS = max \left| \left(\frac{\partial \log_{10} \left| I_{DS(V_{DS,max})} \right|}{\partial V_{GS}} \right)^{-1} \right| \tag{3.2}$$

The OTFT sensor has been utilized for low-range (ppm) ammonia sensing application in ambient atmospheric conditions at RT and 54% RH. The transfer curve plot for low ppm NH_3 sensing has been plotted in **Figure 3.8(a)**. Here solution-processed device offers extraction of multi-parameter in terms of threshold voltage, Trap charge density, mobility subthreshold swing, etc. **Table 3.1** lists the extracted parameters with the exposed NH_3 gas. It has been remarked that the V_{TH} of the OTFT sensor changes from -0.279 V to -0.428 V, and a relatively large change of 42.5 % was observed in the mobility with 5 ppm ammonia gas exposure. The change in V_{TH} and μ_P is due to the increased trapped charge density (Δn_{Trap})

at the sensing surface after ammonia exposure. **Figure 3.8(b)** shows the extracted μ_p and V_{TH} with varying NH_3 concentrations. The trapped charge density can be given by [16]

$$\Delta n_{Trap} = \frac{Q_{Trap}}{q} = \frac{\Delta V_{TH} C_{OX}}{q} \tag{3.3}$$

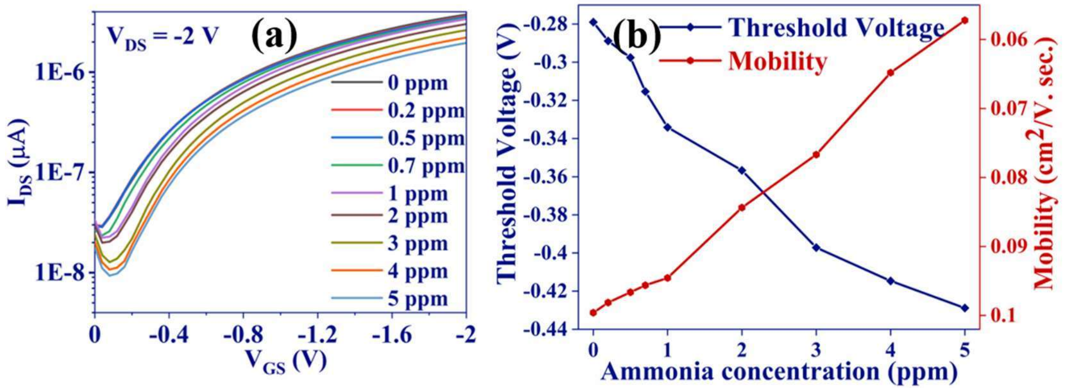

Figure 3.8 (a)Transfer curve plot (I_{DS}- V_{GS}) with varying ammonia concentration (0- 5 ppm), (b) Extracted threshold voltage (V_{TH}), mobility (μ_p) with varying ammonia concentration (0 to 5 ppm).

The sensor has an almost linear sensing response at a low ppm range of ammonia gas. **Figure 3.9(a)** illustrates the linearity of the sensor's response at varied NH_3 concentrations. The fabricated solution-processed OTFT offers an excellent linear relationship with correlation coefficients (R^2) of 0.9965.

Table 3.1 Electrical Parameters with Exposed Ammonia Gas (0 to 5 ppm)

Ammonia gas (ppm)	**Threshold Voltage (V_{TH}) (V)**	**Mobility (μ_P) cm^2 /V. sec.**	**Subthreshold Swing SS (V/dec.)**	**(Q_{trap})** ($\times 10^{11}$/cm^2)	**I_{on} (µA) (V_{GS} = V_{DS}= -2V)**	**Sensing Response S (%)**
0 ppm	-0.27900	0.09959	0.56494	0	-3.75856	0.0
0.2 ppm	-0.28882	0.09813	0.57891	0.2455	-3.62251	3.63
0.5 ppm	-0.29752	0.09663	0.58791	0.46306	-3.54958	5.57
0.7 ppm	-0.31535	0.09562	0.59864	0.90887	-3.45788	8.01
1 ppm	-0.33411	0.09456	0.61144	1.37766	-3.38626	9.91
2 ppm	-0.35669	0.08436	0.62277	1.94229	-3.02122	19.62
3 ppm	-0.39718	0.07668	0.63577	2.95448	-2.61866	30.33
4 ppm	-0.41466	0.06481	0.64977	3.39153	-2.21379	41.10
5 ppm	-0.42886	0.05722	0.65871	3.7465	-1.96686	47.67

3.4.2. Sensing Parameters of the Fabricated Sensor

3.4.2.1. Sensing Response and Detection Limit

The sensor's sensing response is a useful parameter to indicate the sensor's quality in the gas sensing application. The gas sensing response of any OTFT sensor can be defined as [17]

$$S\% = \frac{\left|I_{DS(gas)} - I_{DS(air)}\right|}{I_{DS(air)}} * 100\% \tag{3.4}$$

Where I_{DS}(air) and I_{DS}(gas) represent the drain current in air and gas, respectively. Theoretically, the detection limit (LOD) value can be expressed as [173]

$$LOD = \frac{3\sigma_{rms}}{n} \tag{3.5}$$

The term σ_{rms} stands for the RMS standard deviation of the sensing response plot, and the η stands for the calibrated curve's slope. Graphically, a linear fit of the sensor response at low concentrations of ammonia gas extracts the LOD of the gas sensor. The sensitivity plot in **Figure 3.9(a)** shows a sensing response of 47% at 5 ppm NH_3 analyte, and the detection limit of the sensor is 11.65 ppb.

3.4.2.2. Selectivity and Stability

The selectivity analysis of the OTFT sensor for different interfering analytes was carried out to analyze the selective analysis of the OTFT sensor. The selectivity bar plot for CO_2, CO, Ethylene, CH_4, and NH_3 gas has been indicated in **Figure 3.9(b)**. Clearly, the selectivity bar plot indicates that the fabricated OTFT is selective for the NH_3 analyte. Exposure to NO_2 gas corrodes the device film due to the highly corrosive nature of NO_2, so the fabricated sensor is not suitable for NO_2 detection.

The stability of the fabricated sensor recorded at the 1^{st}, 3^{rd}, 7^{th}, 14^{th}, 21^{st}, and 30^{th} days of the month is plotted in **Figure 3.9(c)**. The sensing response variation at 5 ppm NH_3 gas and drain current in air shown in **Figure 3.9(c)** demonstrate that the fabricated sensor is stable over a month period. A minute change of ~5% in the sensing response of the sensor has been observed at 5 ppm ammonia exposed over a month.

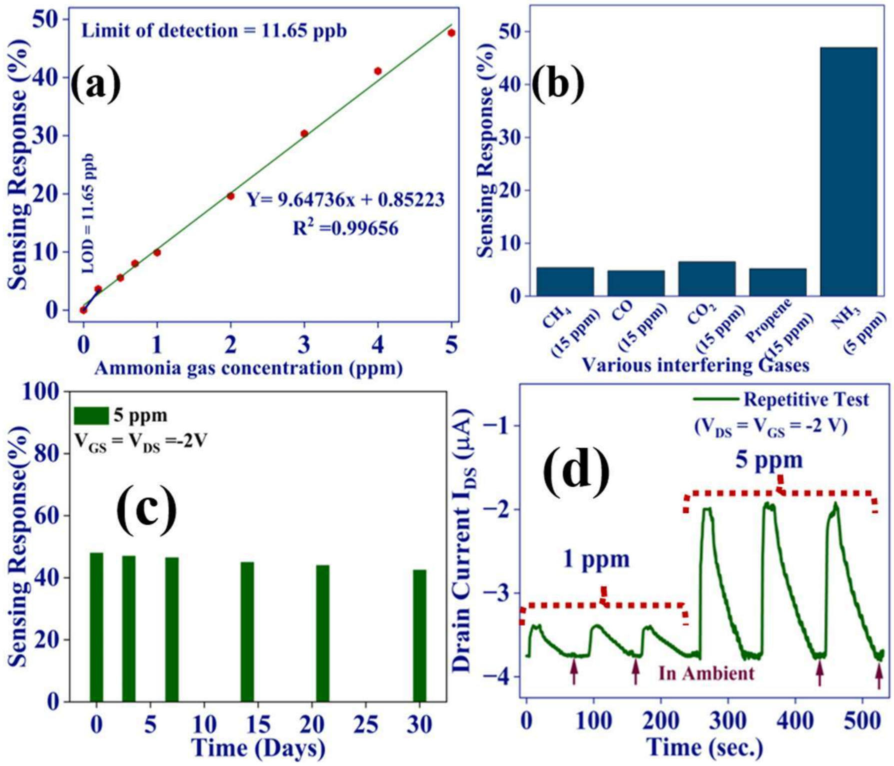

Figure 3.9 (a) Sensing response plot with ammonia concentration range (0 to 5 ppm), (b) Selectivity curve plot for various interfering gases, (c) Sensing response stability at 5 ppm and, (d) Repetitive response of the fabricated sensor.

3.4.2.3. Repetitive Test and Transient Response

The repetitive test and transient response are the important investigation to evaluate the recovery/response time of the fabricated sensor has been plotted in **Figure 3.9(d)** and **Figure 3.10(a)**, respectively. The repetitive test in **Figure 3.9(d)** illustrates that the sensor has good repeatability for exposed ammonia gas. The gas sensor's recovery/response times are usually dependent upon the physisorption or chemisorption mechanism over the sensing film. The physisorption is a surface mechanism of the OTFT sensor, which usually helps to fast doping/de-doping for gas molecules and is favorable for fast gas sensing. On the other hand, chemosorption follows a bulk mechanism and usually takes a long time for doping/de-doping of gas molecules, which is not suitable for fast gas sensing. The average response/recovery time of the fabricated solution-processed OTFT sensor for NH_3 gas was found to be ~9/~50 sec., respectively. The fast sensing is probably due to the dominant physisorption mechanism followed by the fabricated OTFT sensor [174].

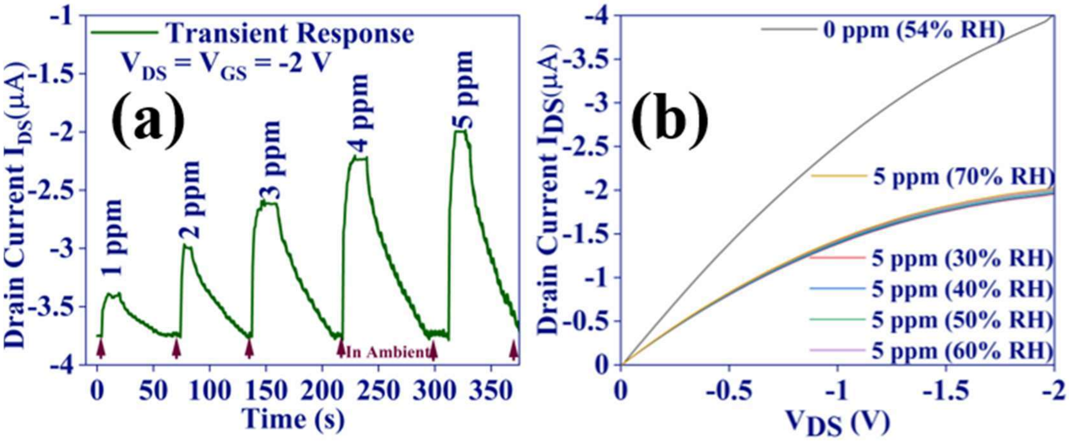

Figure 3.10 (a) Transient response of fabricated sensor (0 – 5 ppm), (b) Drain characteristics with relative humidity variation (30% to 70%).

3.4.2.4. Influence of Relative Humidity on NH_3 sensing

The influence of RH analysis is a critical aspect in determining the gas sensor's quality and reliability for sensing different species of gases. The impact of RH fluctuation on the drain characteristics of the OTFT sensor is indicated in **Figure 3.10(b)**. The fabricated OTFT sensor has been found to be almost insensitive to variations in RH (30% to 70% RH range). The tiny drop in the count of reactive sites for NH_3 gas desorption/ adsorption accounts for the minor variation in the OTFT device's sensing response. **Figure 3.10(b)** depicts a minute variation with RH has been observed in the gas sensor's sensing response at 5 ppm NH_3 gas.

3.4.2.5. Qualitative/Comparative Investigation of Fabricated OTFT Sensor

A comparative/qualitative investigation of the fabricated sensor has been carried out to examine the quality and reliability of the sensor. **Table 3.2** demonstrates that the fabricated OTFT device is a potential candidate in the near future to detect NH_3 analyte at low voltage operation and RT.

Table 3.2 Qualitative/Comparative Investigation of the Fabricated Gas Sensor.

Device Structure	Sensing Element	Method	$T_{Res}/T_{Rec.}$ (sec.)	S%	LOD	O.V. /Temp.	Remarks [Reference]
MO Sensor	Ta_2O_5	MOCVD	495/-	74% (1000 ppm)	0.1 ppm	1.5 V/RT	Very poor and slow response [175]
Chemiresistive	ZnO/PPy	Screen Printing	-	75% (100 ppm)	1 ppm		Poor response, high LOD [126]
Chemiresistive	MoS_2	Electrospinning	80/70	40% (200 ppm)	720 ppb	-/ RT	Poor response and LOD [176]
Chemiresistive	PTB7/ZnO NR	Spin Coating	5/30s	66% (20 ppm)	2 ppm	2/ RT	Poor response and LOD [19]
Optical Sensor	Ag Nanowire	Dip Coating	-	-	1 ppm	-	Complex and costly setup [150]
OTFT sensor	Graphene	CVD	40/120	20% (3 ppm)	-	2 V/RT	Slow response time/relatively poor sensing response [177]
OTFT Sensor	PQT-12/CdSe	FTM	50/200	51% (100 ppm)	-	-40 V/RT	Poor sensing response, response time, high operating voltage [168]
OTFT Sensor	PBTTT	FTM	26/44	89% (100 ppm)	0.33 ppm	-60 V/RT	Poor sensing response, response time, high operating voltage [17]
OTFT Sensor	$P3HT/MoS_2$	FTM	-	63% (100 ppm)	~1 ppm	-60V/RT	Poor sensing response, high operating voltage [16]
OTFT Sensor (Our Work)	P3HT	FTM	9/50	47% (5 ppm)	11.6 ppb	-2V/RT.	High sensing response, low voltage operated, quick response

3.5 Device Physics and Sensing Mechanism

Figure 3.6(a) and **Figure 3.6(b)** indicate the drain curve characteristics and the transfer curve characteristics for a voltage sweep from 0 to -2 V, respectively. It has been noticed that the OTFT can operate at a low voltage of -2 V with a drain current of -3.75 μA. The use of optimized lanthanum doping in ZrOx not only reduces the RMS surface roughness (as shown in AFM morphology in **Figure 3.3(a)** and **Figure 3.3(a')**) but also maintains the capacitance per unit area (indicated in **Figure 3.4(c)**) of the gate oxide film. The capacitance per unit area of the gate oxide film further enhances the current driving capability of the transistor, which is suitable for low voltage operated TFT. The synthesized dielectric offers a high band gap of 5.25 eV and a dielectric constant of 22, which exhibits high dielectric capacitance per unit area of 486 nF/cm^2 at 1 kHz with low leakage current density of ~0.5×10^{-8} A/cm^2 at -2 V. The sensing mechanism towards ammonia gas can be explained with the help of the doping/de-doping phenomenon at the P3HT sensing surface. Each ammonia molecule has a lone pair of electrons; exposure at the sensor's surface causes a change in the device's conductivity by depleting the number of active charge carriers over the sensing film. This is called the trap charge phenomenon at the sensing film, shown in **Figure 3.11(b)**. The ammonia molecule creates an extra Lowest unoccupied molecular orbital (LUMO) level in the P3HT polymer energy level, observed by the Cyclic Voltammogram in **Figure 3.11(a)**. The cyclic voltammogram plot in **Figure 3.11(a)** shows the Highest occupied molecular orbital (HOMO) level of the unexposed P3HT polymer calculated by $E_{HOMO} = -(4.41+Eox(onset))$ eV is -5.09 eV. and excitation energy of 1.62 eV. [178]. The excitation energy increases after ammonia gas exposure due to depleting the number of active carriers, shown in **Figure 3.11(a)** is 1.83 eV. The charge trapping phenomena at the surface of the P3HT polymer produce a decrease in the conductivity of the sensing film by creating an additional LUMO level, and the excitation energy increases. The LUMO level shifted from -3.47 eV. to -3.28 eV. after exposure to ammonia gas, which is calculated in **Table 3.3**. The change in the conductivity due to the trapped charge phenomenon at the polymer sensing film or increase in excitation energy results in the sensing response towards ammonia gas.

The dielectric film also plays a crucial role in enhanced gas sensing. A suitable smoother dielectric film or dielectric film surface modifications (HMDS treatment) improves the dielectric/semiconductor interface property, offers low trap charge density for charge carrier transport (due to smoother dielectric surface), which controls the morphology of sensing film, dielectric/semiconductor interface properties, and grain boundaries of the organic semiconductor channel, suitable for a high-performance gas sensor [179][180]. The structural morphology of the sensing surface in AFM **Figure 3.3(c)/(c')** shows that the film offers a high average surface roughness of 4.2 nm. A high average roughness of the organic semiconductor sensing film provides more adsorption/ desorption sites or a high surface area/volume ratio for ammonia gas molecules, enhancing the sensor's sensing response [168]. Moreover, the FTM-deposited P3HT polymer shows a crystalline and highly oriented grain of the polymer film, which improves chain ordering and grain stacking of the organic semiconductor channel. Further, the improved chain ordering and grain stacking enhance the π-π electron delocalization and charge transport phenomenon in the organic semiconductor channel, which improves the sensor's response/recovery time and sensing performance. The charge trapped at the sensing layer due to ammonia molecules interaction behaves like a defect in the lattice, which increases the threshold voltage (~54% relative change for 5 ppm NH_3 gas), reduces the mobility (~47% relative change for 5 ppm ammonia gas) of the transistor (Refer to **Figure 3.8(b)**) upto a large scale, resulting a large change in the drain current, thereby enhancing the response of the sensor [181].

Table 3.3 Electronic Parameters Extracted from CV Plot

Sensing Surface	**HOMO**	**LUMO**	**E. E. (eV.)**
P3HT before Exposure	-5.09 eV.	-3.47 eV.	1.62 eV.
P3HT after Exposure	-5.11 eV.	-3.28 eV.	1.83 eV.

* HOMO – LUMO = Excitation Energy, E.E. – Excitation Energy

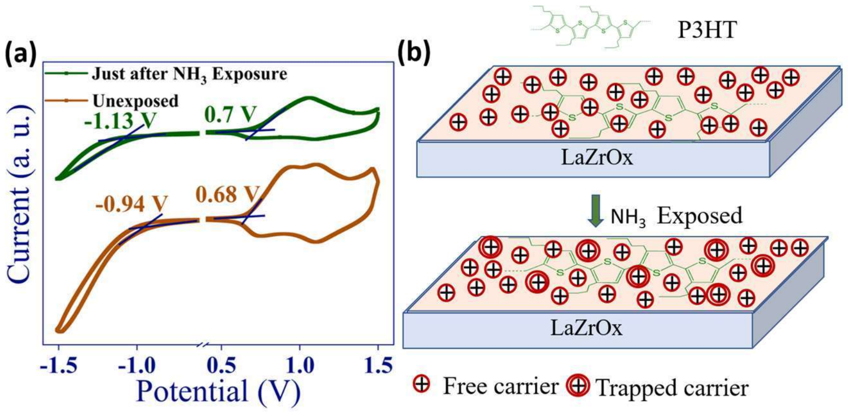

Figure 3.11 (a) Cyclic Voltammogram plot of unexposed P3HT sensing film and ammonia exposed P3HT sensing film, (b) Ammonia interaction over the P3HT sensing surface.

3.6 Conclusion

The present work aims to fabricate a fully solution-processed cheap organic TFT sensor for ammonia sensing utilizing P3HT polymer as an active layer. In the current work, a high-k dielectric constant (~ 22 at 1 kHz) based on inorganic gate oxide, LaZrOx, has been developed and used to fabricate a low voltage (~ -2 V) operated OTFT sensor. A thin uniform oxide film (40±3 nm) with good electrical insulation has a good capacitance per unit area of 486 nF/cm^2 at 1 kHz frequency and a leakage current density of ~0.5× 10^{-8} A/cm^2 (at -2 V), making it suitable for low voltage OTFT sensors. A simple, cost-efficient FTM (floating film transfer) method has been used to coat a uniform film thickness of 25±4 nm active polymer film on the solution-processed LaZrOx/HMDS film. At room temperature (RT), the solution-processed OTFT is a viable choice for low-concentration NH_3 sensing and is almost independent of the relative humidity (RH) factor. At 5 ppm ammonia gas, the sensor has a high response of 47% and a short average response and recovery time of 9 and 50 seconds, respectively. The current study shows that fabricating a low-cost solution-processed organic TFT for a highly toxic NH_3 analyte at RT is feasible.