

# **FABRICATION AND CHARACTERIZATION OF ORGANIC THIN FILM TRANSISTORS FOR AMMONIA SENSING APPLICATION**



**Thesis submitted in partial fulfillment  
for the Award of Degree**

## **DOCTOR OF PHILOSOPHY**

BY

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**ROLL No. 18091003**

**2023**

## **CHAPTER-6**

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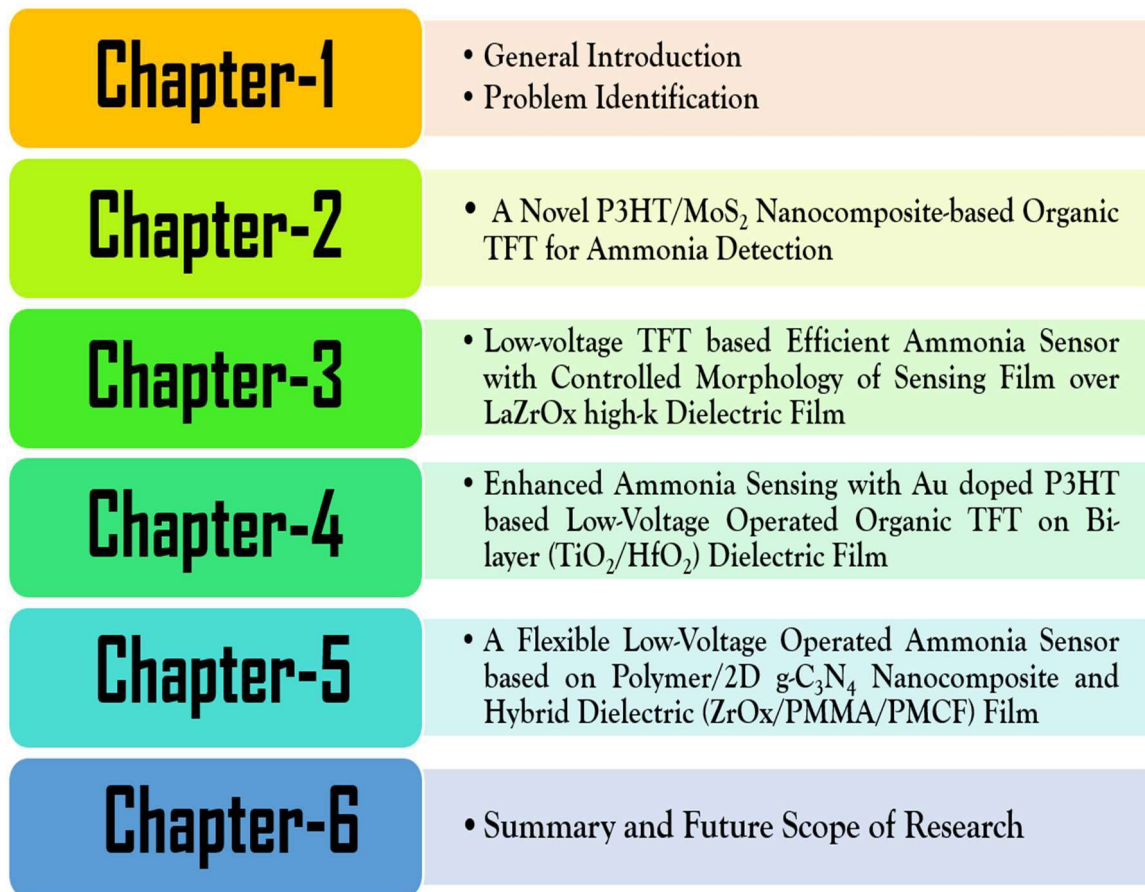
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### ***Summary and Future Scope of Research***

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**Figure 6.1** Thesis chapter outlines.

The main contribution of the thesis is illustrated in **Figure 6.1**. In the era of electronic industries, thin film transistors (TFTs) find extensive applications in various electronic and sensing fields. The present thesis explores the significant contribution of TFTs in ammonia gas sensing applications. The thesis covers various complexities in the device fabrication steps and also explores the floating film transfer method along with precautions to mitigate these complexities during the device fabrication.

The present thesis also includes various cost-efficient solution-processed low-voltage operated ammonia sensing devices on rigid silicon and flexible ITO PET substrate. Mainly, the utilization of high-k dielectric materials as a gate oxide in the fabrication of TFT devices has

introduced a significant reduction in operating voltage. This advancement enables their application in low-power electronic applications. The thesis presents cost-effective solution-processed fabrication techniques for developing low-voltage operated TFTs. These techniques will open up new research avenues in the field, eliminating the need for expensive equipment. The thesis's findings will spur design engineers to fabricate different organic TFTs that can detect ammonia and various gases at room temperature operation.

## **6.1 Chapter-Wise Summary**

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Chapter 1 presents as the introduction, encompassing a brief literature review covering the fundamentals of organic semiconductors, the charge transport mechanism in organic semiconductors, and the use of high-k dielectrics in organic thin film transistors. This chapter also includes the basic working principle of thin film transistor and their application in ammonia gas sensing. In this chapter, we have discussed various complexities and issues related to high-k dielectric deposition and the adoption of unique techniques to address these challenges. This discussion aims to provide new readers with a preliminary understanding of the concepts involved in the fabrication process.

Chapter 2 reports the fabrication and characterization of P3HT/MoS<sub>2</sub> nanocomposite-based TFT for ammonia gas sensor. The essential highlights of the chapter are as follows.

- 1) The device fabrication uses a low-cost self-assembled Floating Film Transfer (FTM) method for the deposition of the P3HT/MoS<sub>2</sub> nanocomposite matrix.
- 2) The surface morphologies of the synthesized polymer nanocomposite film are characterized with the help of AFM, XRD, UV-Vis spectroscopy, etc.

- 3) The surface morphology of the P3HT/MoS<sub>2</sub> nanocomposite matrix forms a nanoribbon structure, which enhances the charge transport phenomenon in the active channel.
- 4) The device possesses a sensing response of 63% at 100 ppm ammonia gas.
- 5) The fabricated device is almost independent of relative humidity variation.

Chapter 3 envisages a low-voltage operated TFT using a P3HT polymer film on a LaZrOx/HMDS/Si substrate. This work explores the role of dielectric/semiconductor interface for enhanced ammonia sensing characteristics at room temperature. The significant findings of this chapter are summarized below:

- 1) The Pristine P3HT on LaZrOx dielectric-based Organic TFT has been explored for ammonia sensing application.
- 2) The dielectric film has been optimized for a smooth surface and high dielectric constant with the optimized ratio of lanthanum acetate and zirconium acetylacetonate solution.
- 3) The dielectric film offers the following advantageous parameters.
  - ❖ High band Gap (5.25 eV.) – suitable for gate oxide material as it suppresses the thermionic emission in the dielectric film.
  - ❖ High dielectric Constant (k- 22 and C<sub>d</sub> - 486 nF/cm<sup>2</sup>) – suitable for low voltage operation of the device.
  - ❖ Low leakage current density (0.5×10<sup>-8</sup> A/cm<sup>2</sup>) at -2 V implies that there are very few or no pinholes in the dielectric film.

- 4) The device has the ability to operate at -2 V of  $V_{DS}$  and  $V_{GS}$  supply voltages with a good saturated current of  $\sim 3.75 \mu A$ , and an enhanced field effect mobility of  $0.1 \text{ cm}^2/V \cdot \text{Sec}$ .
- 5) The synthesized dielectric film controls the film orientation, growth, and morphology of the pristine P3HT film, which is beneficial for high-performance OTFT sensor.
- 6) The synthesized P3HT film on the LaZrOx dielectric film offers a nanostructure with connected grains and a high surface roughness of 4.2 nm, which provides a high surface-to-volume ratio for enhanced ammonia sensing.
- 7) The sensor has an almost linear sensing response at a low ppm range of ammonia gas and a good linearity correlation coefficient of 0.9965.
- 8) The fabricated ammonia sensor shows a sensing response of 47% at 5 ppm  $\text{NH}_3$  analyte with a detection limit of 11.65 ppb, and is almost stable over a month.
- 9) The fabricated sensor follows the dominant physisorption phenomenon with a short average response/recovery time of  $\sim 9/\sim 50 \text{ sec}$ ., for ammonia gas, respectively.
- 10) The sensor exhibits almost no dependence on the relative humidity factor (30%-70%) and demonstrates a high degree of repetitive response to ammonia gas.

Chapter 4 presents the utilization of a bilayer high-k dielectric ( $\text{TiO}_2/\text{HfO}_2$ ) to fabricate an Au (gold)-doped P3HT-based thin film transistor for a fast and enhanced performance ammonia sensor. The device can work at a low voltage, which can be further used in various low-power electronic applications in the future. The summary of the work is as under.

- 1) The device fabrication utilizes a low-cost, self-assembled floating film transfer (FTM) technique for organic semiconductor growth, and the synthesized bilayer dielectric has been obtained through thermal annealing of a spin-coated film.
- 2) The surface morphologies of the synthesized bilayer dielectric film and the Au nanoparticle-doped P3HT polymer nanocomposite film are characterized using AFM and XRD.
- 3) TiO<sub>2</sub> film with a thickness of  $17 \pm 3$  nm, and HfO<sub>2</sub> film with a thickness of  $21 \pm 4$  nm, in the synthesized bilayer dielectric film, offers a high areal capacitance of  $0.926 \mu\text{F}/\text{cm}^2$  with a high dielectric constant of  $\sim 42$ .
- 4) The dielectric band gap of the synthesized bilayer dielectric is 5.6 eV. which is sufficient to suppress the leakage current of the dielectric layer to  $1 \mu\text{A}$  at a -6 V supply.
- 5) The RMS surface roughness of the dielectric film is 0.915 nm, indicating a smooth film that suppresses the carrier scattering at the semiconductor/dielectric interface in the fabricated OTFT. While on the other hand, the average surface roughness of the synthesized Au/P3HT film is 1.732 nm, providing a large number of active sites for gas adsorption/desorption and contributing to enhanced gas sensor performance.
- 6) The device shows a low subthreshold swing of 509.4 mV and offers a high current of  $8.59 \mu\text{A}$  at  $V_{\text{GS}} = V_{\text{DS}} = -1.5$  V supply.
- 7) The apparent threshold voltage of OTFT,  $V_{\text{TH}}(\text{V})$  is found to be 0.1539 V for the ambient air (0 ppm Ammonia) condition, and its changes to 0.4980 V after exposure of 5 ppm concentration of ammonia gas. This shift in the threshold voltage

occurs because of the trap charge carriers present over the sensing surface.

- 8) The sensing device with a high sensing response of 55.66 % over 5 ppm ammonia gas in a room temperature operation is highly stable over a month.
- 9) The device with a quick response ( $T_{res.}$ )/recovery ( $T_{rec.}$ ) time of 6/17 sec. is almost independent of relative humidity variation.
- 10) The incorporated Au nanoparticle enhances the polymer-metal nanoparticle crosslinking, sensing performance, and stability of the fabricated sensor.

Chapter 5 is the continuation of the Chapter 3 work, but with a different substrate and fabrication technique. This chapter explores ammonia sensing applications with a fabricated low-voltage, flexible organic thin film transistor. The summary of the chapter is summarized as follows.

- 1) The P3HT/g-C<sub>3</sub>N<sub>4</sub> organic semiconductor nanocomposite film, synthesized with low-cost FTM, has been deposited over low-temperature UV- cured spin-deposited hybrid dielectric film (ZrO<sub>x</sub>/PMMA/PMCF) in the fabrication of flexible thin film transistor for ammonia gas sensor.
- 2) The UV-cured synthesized dielectric film offers low-temperature processability of the hybrid dielectric film for the fabrication of low-voltage flexible TFT.
- 3) The device has the ability to operate at -2 V supply because of the high-k hybrid dielectric, which has an aerial capacitance of 310 nF/cm<sup>2</sup> at 1 kHz.
- 4) The hybrid flexible dielectric has a band gap of 5.27 eV., sufficient to suppress the gate leakage current.
- 5) The dielectric layer (15 mm×20 mm) with RMS surface roughness of 0.388 nm has excellent bending capability upto a radius of 10 mm. The bending performance of

the layers is reversible, i.e., no permanent changes have occurred with the applied bending stress.

- 6) A shift of 25 mV in threshold voltage ( $V_{TH}$ ) and drain current shift from  $\sim 2 \mu$  to  $\sim 1.8 \mu$ A with a 10 mm bending radius, which confirms the acceptable bending performance of the fabricated flexible OTFT.
- 7) The fabricated device has a high sensing response of 69% at 20 ppm ammonia gas, and the sensing response with exposed analysis is highly correlated with a correlation coefficient of 0.988.
- 8) The threshold voltage ( $V_{TH}$ ) shifts from 0.1052 V to 0.3520, and a 61.7% relative change in the field effect mobility ( $\mu_p$ ) has been observed with a 20 ppm exposed target analyte.
- 9) The fabricated selective ammonia sensor exhibits a fast average response time of 4.7 seconds and an average recovery time of 38.62 seconds. It is almost independent of the relative humidity factor.
- 10) The incorporation of 2D g-C<sub>3</sub>N<sub>4</sub> in planarized polymer chain enhances nucleation growth with fewer defects and vacancies, resulting in better  $\pi$ - $\pi$  interaction on the nucleation sites. This incorporation leads to faster and improved sensing performance of the sensor.
- 11) The exposed target gas changes the bandgap of the polymer nanocomposite film from 1.89 eV. to 2.06 eV. due to ammonia creating an additional LUMO level by means of charge trapping over the polymer nanocomposite sensing surface.

The finding and comparison between performed works have been summarized in the .

**Table 6.1.**

**Table 6.1** Performance Comparison between Performed Works

Parameters	P3HT/MoS <sub>2</sub> TFT for NH <sub>3</sub> Sensing	P3HT with LaZrOx dielectric TFT for NH <sub>3</sub> Sensing	Au/P3HT with Bilayer dielectric TFT for NH <sub>3</sub> Sensing	P3HT/2D-gC <sub>3</sub> N <sub>4</sub> with Hybrid dielectric TFT for NH <sub>3</sub> Sensing
<b>Sensing Material</b>	P3HT/MoS <sub>2</sub>	P3HT	Au/P3HT	P3HT/g-C <sub>3</sub> N <sub>4</sub>
<b>Oxide/Dielectric Layer</b>	SiO <sub>2</sub>	LaZrOx	TiO <sub>2</sub> /HfO <sub>2</sub>	ZrOx/PMMA/PMCF
<b>OSC Deposition Technique</b>	FTM	FTM	FTM	FTM
<b>Dielectric Deposition Technique</b>	Dry Oxidation	Spin Coating	Spin Coating	Spin Coating
<b>Dielectric Deposition Temperature</b>	1100 °C	625 °C	500 °C	100 °C
<b>Dielectric Constant</b>	3.9	~22	~42	~20
<b>Dielectric Bandgap</b>	~9 eV.	~5.25 eV.	~5.6 eV.	~5.27 eV.
<b>Areal Capacitance</b>	~10 nF/cm <sup>2</sup>	~ 486 nF/cm <sup>2</sup>	~0.926 μF/cm <sup>2</sup>	~310 nF/cm <sup>2</sup>
<b>Operation Voltage</b>	-60 V	-2.0 V	-1.5 V	-2.0 V
<b>Threshold Voltage</b>	-3.78 V	-0.28 V	-0.1539 V	-0.1052
<b>Sensing Response</b>	63% (100 ppm)	47% (5 ppm)	55% (5 ppm)	69% (20 ppm)
<b>Correlation Coefficient</b>	0.9964	0.99656	-	0.98862
<b>LOD</b>	904 ppb	11.6 ppb	15.15 ppb	500 ppb
<b>Response Time</b>	-	9 sec.	6 sec.	4 sec.
<b>Recovery Time</b>	-	50 sec.	17 sec.	38 sec.
<b>Nature of Substrate</b>	Rigid Silicon	Rigid Silicon	Rigid Silicon	Flexible ITO PET

## 6.2 Future Scope of Research

The thesis that is being presented here cannot be expanded upon because Ph.D. work is a time-limited program. However, the study described here can open new opportunities for doing additional research studies in this field. For example, one can fabricate a low-voltage flexible TFT device with enhanced stability with suitable nanocomposite material for dielectric and organic semiconductor channel layers. Transparent and flexible electronics are currently in great demand in the market, both in consumer electronics and in scientific applications. The researchers will be inspired to try their applications in other fields by the work shown here for fabricating various devices with organic materials. Based on the study

reported in Chapter 2, a few directions for the field's future research are listed below.

- ❖ A few other high-k dielectrics may be tried for low-voltage operated OTFT.
- ❖ The performance of P3HT/MoS<sub>2</sub>-based OTFT sensors for gas sensing can be implemented with other nanotechnology (nanoparticles or quantum Dots).
- ❖ Future optoelectronic applications can be accomplished with the merging of OTFT and OLED on a single platform.
- ❖ The electrode material such as Palladium, Platinum can be tried for better performance of the sensing device.

The studies discussed in Chapter 3 are anticipated to spur researchers to conduct additional research in the following areas.

- ❖ The thermally annealed dielectric can be processed by other low-temperature-synthesized techniques (ALD, E-Beam Deposition, Sputtering) for flexible PET, PDMS, and plastic substrate.
- ❖ Rare earth metal as a dopant in the P3HT polymer matrix to improve performance in gas sensing may be tried.
- ❖ The developed high-k dielectric material can be further tried with other active semiconductor materials to fabricate low-voltage OTFT and can be used in various optoelectronic and sensing applications.

The scope of Chapter 4 can further be extended in order to realize the complementary organic-based TFT, which can be made by choosing proper n-type and p-type materials. Some key possibilities can be realized with the help of an organic platform.

- ❖ A flexible polymer OTFT sensor can be realized with PET, polyamide, PEN, cello

tapes, clothes, etc., for future wearable and smart sensor technology.

- ❖ Other suitable high-k dielectric materials can further enhance the performance of the bilayer high-k dielectric-based organic TFT to reduce the operating voltage of the TFT and enhance the drain current of the organic TFT.
- ❖ The OTFT and OLED integration on a single platform can be realized for future optoelectronic applications.
- ❖ A ternary compound organic semiconductor channel (Metal nanoparticle doped polymer nanocomposite material) can further improve the performance of the organic device.
- ❖ Fabricated low-voltage devices can be further used in the fabrication of low-power logic gates, inverters, and memories.

The scope of Chapter 5 has a vast application in the area of electronic and sensing applications that can further be extended in order to realize the organic-based TFTs. Some of the key scopes are pointed out below-

- ❖ The dielectric areal capacitance of the synthesized UV-Cured dielectric film is lower compared to thermally annealed dielectric film. One can improve the densification and dielectric areal capacitance with other suitable vacuum deposition techniques to improve the performance of the device.
- ❖ The fabricated flexible device can be further extended to fabricate a wearable low-power smart sensor in nearby future.
- ❖ The bending or flexible properties of the fabricated flexible sensor can be further enhanced by suitable polymer dielectric material dopant in a high-k inorganic

dielectric material.

- ❖ The fabricated flexible device can pave the way for new low-cost, simple fabrication techniques for low-voltage, low-power operated devices for a variety of applications, including optoelectronics, gas sensing, flexible memories, and medical applications. It can also be further developed to create a wearable low-power smart sensor in the near future.

Although a significant amount of remarkable research has been conducted to fabricate thin film transistors for various electronic and sensing applications, the future scope of the work described above is in no way limited. Further research, accompanied by additional theoretical analysis, including compact modeling, can maximize the performance of TFTs for the intended applications. For example, a modified TFT structure known as an Organic-based Electrochemical Transistor (OET) can be employed in various medical applications and biosensing, enabling the detection of biomolecules, bacteria, viruses, glucose levels, blood tests, and more.