1.1 Thesis Abstract

The importance of gas sensing technologies has grown significantly due to their role in monitoring environmental contaminants and maintaining safety across a range of applications. The present study investigates the advancement and utilization of gas sensors utilizing organic field-effect transistors (OFETs). Organic semiconductors possess distinct benefits, such as their inherent flexibility, cost-effectiveness in manufacturing, and the ability to customize their chemical sensing capabilities. The research starts by undertaking the design and manufacture of gas sensors based on organic field-effect transistors (OFETs), employing organic semiconductor materials. The sensing method is dependent on the change in the mobility of charge carriers inside the transistor channel, which occurs as a result of particular interactions with gases. The selection of organic materials is meticulously evaluated in order to optimize sensitivity and selectivity towards certain gases of interest. The primary objective of experimental research is to analyze and evaluate the sensor's reaction to various gases, encompassing volatile organic compounds (VOCs) as well as prevalent environmental contaminants. The sensors demonstrate exceptional performance for Hydrogen sulfide gas sensing in terms of their sensitivity, response time, and recovery properties. The investigation also includes the examination of the impact of environmental variables, such as temperature and humidity, on the functioning of sensors. Moreover, the study investigates the improvement of sensor characteristics, including channel and gate dielectric properties, in order to improve the overall performance of the sensor. The objective is to develop a gas sensing platform that is both dependable and replicable, making it ideal for practical use in real-world scenarios. The advantages of OFET-based sensors, such as their potential for downsizing and integration into flexible electronic devices, are underscored through a comparative study with existing gas sensing

technologies. In summary, this research makes a valuable contribution to the progressing domain of gas sensing by showcasing the viability and prospects of gas sensors based on organic field-effect transistors (OFETs). The results of this study offer valuable information on the enhancement of sensor performance and lay the foundation for the creation of innovative, adaptable, and affordable gas sensing platforms. These platforms have the potential to be utilized in several fields, such as environmental monitoring, industrial safety, and healthcare.

1.2 A Brief History and Overview of Gas Sensors

Gas sensors play a pivotal role in monitoring and detecting the presence of various gases in our environment, serving a wide range of applications from industrial processes to environmental safety [1][2]. These sensors are crucial for ensuring the well-being of both humans and the planet by providing early warnings about potential hazards and facilitating efficient control of processes. The evolution of gas sensors spans a fascinating journey, marked by advancements in technology, materials, and ongoing efforts to safeguard human lives and the environment from the potential dangers posed by hazardous gases. Here's a brief overview of key milestones in the history of gas detection:

Early 19th Century: The earliest forms of gas detection were rudimentary and often relied on human senses. Miners, for example, used canaries to detect the presence of toxic gases in coal mines. If the canary showed signs of distress, it signaled the presence of harmful gases like carbon monoxide.

Late 19th Century: The development of chemical indicators marked an early step in gas detection. These indicators, often paper strips impregnated with reactive substances, changed color in the presence of specific gases.

Early 20th Century: The introduction of flame safety lamps in coal mines provided a

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In regard to take a step closer towards the problem statement identified in Chapter 1, in the current article, we have investigated a highly selective, sensitive, low-power, and cost-efficient H_2S gas sensor utilizing the thin film of conjugated organic polymer Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b; 3,4-b'] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) as an active sensing layer. The organic thin film of PCPDTBT polymer is developed using a cost-effective, facile solution-processed floating film transfer method (FTM). Additionally, state-of-the-art technique used for annealing named 'solvent vapor annealing' offers enhanced crystallinity, excellent charge transfer along the polymer chain which, significantly improves sensitivity. The fabricated organic field effect transistor (OFET) with Top contact bottom gate (TCBG) configuration is thoroughly explored to investigate the thin film's electrical and gas sensing performance for toxic and hazardous H_2S gas. The fabricated device worked at room temperature (RT-25 ºC) and was highly sensitive to the presence of H_2S gas at concentrations even lower than 1 ppm. The fabricated OFET device has excellent air stability, good response–recovery behavior (response/recovery time of 8/250 sec, respectively), exceptional gas response reproducibility, and a high sensor response of 71.3% at 1 ppm H_2S gas exposure.

2.1 Introduction

Hydrogen sulfide (H_2S) is a colorless, highly toxic, corrosive, hazardous, and flammable gas at ambient conditions. According to Occupational Safety and Health Administration (OSHA), after carbon monoxide (CO), hydrogen sulfide (H_2S) is one of the most hazardous chemicals in the workplace [61]. Since H_2S gas is denser than ambient air and can easily accumulate in enclosed spaces at or below ground level, making these

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In previous chapter the developed sensor has demonstrated poor recovery characteristics, environmental degradation, significant reliance on relative humidity variation, less mobility, and a possibility to further enhance the sensing response. In regards to improve all these parameters, the nanocomposite of organic-inorganic material has been utilized. The synergistic effect between these two classes of materials helped in improving the stated parameters. Further, photoirradiation of composite solution has facilitated the molecular ordering of the polymer composite matrix, which further enhanced the charge transport properties of the sensing layer. In present work, a facile method to develop PCPDTBT/CdS composite thin film with the integration of photoirradiation of the nanocomposite solution, simple and inexpensive floating film transfer deposition method (FTM), and solvent vapor annealing (SVA) has been demonstrated. The film is applied to organic field-effect transistor (OFET) in top contact bottom gate (TCBG) configuration, to evaluate the gas sensing performance for various concentrations of reducing and toxic H_2S gas, at room temperature. Synergetic effect of the photoirradiation, presence of CdS, FTM, and SVA enhances the molecular ordering of the polymer matrix. Photoirradiated PCPDTBT/CdS nanocomposite film exhibits a maximum charge carrier mobility of ~$3.4*10^{-3}$ cm^2/V. s, which is many folds higher than the pristine PCPDTBT film. Favourable π-π and electrostatic interactions after photoirradiation and self-aligned nature of FTM film enhances the interfacial interactions between CdS and PCPDTBT. Additionally, state-of-the-art technique 'solvent vapor annealing' offers enhanced crystallinity, excellent charge transport along the polymer chain which, significantly improves sensitivity. Photoirradiated-SVA annealed PCPDTBT/CdS composite film based OFET sensors consistently show enhanced sensitivity compared to the pristine PCPDTBT, and

PCPDTBT/CdS composite. Particularly, the photoirradiated-SVA annealed PCPDTBT/CdS composite sensor achieves significantly enhanced response of ~81% to 1 ppm exposure of H_2S gas, compared to the pristine PCPDTBT (~71%), and PCPDTBT/CdS (~76%) nanocomposites. Additionally, excellent response-recovery behaviour (e.g., ~5 s and ~ 90 s, respectively), good ambient stability, and excellent selectivity are also observed.

3.1 Introduction

To date, numerous organic polymer (Polyaniline, Polypyrrole, Polyphenylene, Polyacetylene, P3HT, PBTTT, PQT-12, etc.), semiconducting inorganic materials (metals, metal oxides, transition metal disulfides, monosulfides, etc.), and doping techniques have been used to enhance the film morphology and improve electrical conductivity and sensitivity in an effort to improve H_2S gas-sensing performance [84][85]. These organic and inorganic semiconductor-based hydrogen sulfide gas sensors have accomplished excellent research improvements in terms of good sensitivity, better selectivity, and quick response/recovery properties [51], [86]–[89]. Furthermore, organic materials have issues related to low conductivity, poor ambient stability, and strong affinity to volatile organic substances [90] and inorganic materials possess the limitations in terms of high-temperature operation, solid-substrate limit, poor selectivity, and complicated processability [91]. These limitations hinder their use in highly efficient gas sensor fabrication. Moreover, using a nanocomposite of an organic semiconducting polymer and an inorganic material to produce extremely effective gas sensors has drawn a lot of interest in gas-sensing applications because of their synergistic effects. These synergistic effects in organic-inorganic composite enable to eradicate their inherent flaws while also incorporating the merits of their organic and inorganic counterparts in gas-sensing applications, leading to the development of highly effective materials for gas sensors [92]. The synergistic

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In chapter 3, various shortcomings of chapter 2 have been improved significantly. It is essential nowadays to develop low power consumption devices. In this regard, it is necessary to develop the sensor to operate at low voltage. To solve this problem, in this chapter the SiO_2 dielectric layer has been replaced by high-k dielectric material. Further, there is also scope left for improvement in all the sensing parameters obtained in chapter 3. Therefore, we have reported a highly efficient, low-voltage, and cost-effective H_2S gas sensor utilizing the nanocomposite thin film of conjugated organic polymer Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b; 3,4-b'] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and inorganic material (MoS_2) as an active sensing layer. To enhance the molecular ordering of the polymer chains in composite solution, photoirradiation method has been employed. Facile, inexpensive, and solution-processed floating film transfer method (FTM) is used to fabricate the nanocomposite thin film of PCPDTBT/MoS_2. Furthermore, the state-of-the-art annealing method known as "solvent vapor annealing" provides im-proved crystallinity and excellent charge transfer throughout the polymer chain, which substantially enhances the gas sensing performance. High-k dielectric film of $HfLaO_x$ was deposited using the precursors of Hf and La, and spin coat-ing deposition method. The dielectric film exhibited a smooth, pin-hole free, and uniform nature with a very low rms roughness of 0.18 nm and excellent dielectric properties such as high bandgap (5.2 eV), low leakage current density (100 nA/cm^2 at -5 V), and high-k (24.8). To evaluate the thin film's electrical and gas detecting capabilities for harmful and dangerous H_2S gas, a top contact bottom gate (TCBG) organic field effect transistor (OFET) was fabricated. The device was exceptionally responsive to the

presence of hydrogen sulfide gas at concentrations even lower than 1 ppm and operated at room temperature (RT). The developed OFET device exhibits outstanding air stability, excellent response-recovery behavior, outstanding gas response repeatability, and a sensor response of 93.2% at 1 ppm exposure of H_2S gas. Response/recovery times are 4/55 seconds, respectively.

4.1 Introduction

OFETs (organic field-effect transistors) have made significant advancements and are of critical importance for applications in next-generation electronics. Power consumption is one of the key problems that requires being addressed for the industrialization of the OFETs. The development of OFETs necessitates an advancement of gate dielectric materials that are suitable for low power consumption. These materials must demonstrate exceptional electrical characteristics such as large capacitance, an exceptionally high breakdown strength, and a minimal leakage current density. Historically, the favoured gate dielectric material has been traditional silicon dioxide (SiO_2), but its relatively low dielectric constant does not meet the performance criteria for the aforementioned OFETs. OFETs with a low-voltage operation are required, and numerous progressively developed solutions have drawn a lot of interest from researchers in an effort to accomplish this. The source-drain current of a FET is dependent upon the oxide capacitance, generally described as:

$$C = k\frac{A\varepsilon}{d}$$

Where ε, d, k, and A are the free space permittivity, oxide thickness, relative dielectric constant, and area respectively. From the above equation, we can observe that the gate capacitance can either be increased by reducing the dielectric thickness or increasing the dielectric constant. Direct tunnelling phenomenon of the electrons causes the oxide