Experimental Characterisation of BGBC OTFT for Indoor CO_2 Gas Sensing

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Abstract. Global warming is a concern nowadays due to excessive release of harmful gasses to the environment, leading to greenhouse effect phenomena worldwide. Based on the data provided by global pollution agencies, the release of greenhouse gasses to the atmosphere is the main cause of pollution and the increase in atmospheric temperature due to warming. Greenhouse gasses (GHGs) contents released to the environment is worrying, with carbon dioxide (CO_2) is reported at the highest concentration compared to other gasses. There are many studies conducted to develop and evaluate the performance of harmful gas sensors incorporating inorganic and organic semiconductive materials. Organic semiconductors (OSCs) are environmentally friendly materials, relatively cheaper technology, and comprised of a wide range of materials with good carrier mobility. Therefore, in this work, Organic Thin Film Transistor (OTFT) is developed for gas sensor application. As global warming is becoming more serious, this solution is instead a sustainable solution to the environment, as organic molecules which are held together via Van der Waals bond are easily processed via low-temperature deposition and solution processing as compared to more complicated processes involved in conventional inorganic counterpart. In addition, the developed sensor is generally robust due to the ability to withstand high humidity conditions and can be fabricated on flexible substrates. In this work, suitable materials are identified in basic OTFT construction, which are the electrodes, dielectric and substrate. The scope is mainly focusing on the development of bottom gate OTFT construction, incorporating p-type active material which are Trisisopropylsilylethynyl Pentacene (TIPS Pentacene), Aluminium (Al) as drain and source electrodes, PEDOT: PSS as gate electrode and Polyvinyl alcohol (PVA) as gate dielectric. The materials in bottom gate bottom contact (BGBC) configuration, fabricated via screen printing technique is experimentally tested towards CO_2 detection. CO_2 is initially detected at 1618 ppm with contact resistance of 15 kΩ, and at 10 ml/minute flow rate, the developed configuration is demonstrated able to achieve sensitivity of 2.069 Ω/ppm. In conclusion, the studied BGBC OTFT has demonstrated suitability and applicability in CO_2 gas sensing for sustainable environmental condition monitoring, that could lead to safer environment for the living things on earth. With the proposed dimensions, in the future it is possible to proceed with this work to be fabricated by using more advanced techniques such as photolithography and many others.

Introduction

Increasing release of GHGs to the atmosphere is a leading factor that contributes to global warming. Different human activities such as transportation, plantation, deforestation, industrial and various residential area activities have increased the level of GHGs greatly. Since the start of industrial revolution in the early 1800s, the burning of fossil fuels has greatly amplified the level of GHGs in the atmosphere, especially CO_2, which is also used in fire extinguishers, carbonating drinks, refrigerators, and plant photosynthesis. This gas absorbs infrared (IR) radiation causing no IR reflection to outer space. This results in gradual heating of earth atmosphere and surface via a process referred to as global warming. As sunlight reaches the earth surface, some of it is absorbed which warms the ground and some are reflected to the space as heat. Excessive amount of GHGs in the atmosphere prevent this process, and heat remains in the atmosphere and results in world climate changes.

OTFT has sparked research interests as sensors. A thin OSC film, an insulator, and three electrodes called the source, drain and gate, and a layered structural architecture are used to create an OTFT. The charge carriers are injected and extracted via the source and drain electrodes, which are in contact with the active layer. On the other hand, an insulator that regulates the channel's conductivity separates the gate from the semiconductor sheet. BGBC configuration, as seen in Figure 1, causes the OSC to be in direct contact with the target analytes since large surface area is exposed to them. Similar to how charge builds up in a bulk semiconductor, the channel in an OTFT is created through accumulation. When a bias is applied between the gate to source voltage, V_{GS}, a sheet of mobile charge carriers accumulates near the semiconductor interface that permits current to flow through the active layer when a suitable drain to source potential, V_{DS} is applied. This is how an organic transistor functions as a voltage-controlled-current source. The threshold voltage, V_T is a minimal gate voltage necessary for charge carrier accumulation at the OSC interface.

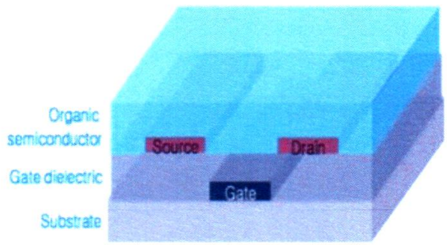


Figure 1. BGBC Configuration for OTFT [1]

Before applying voltage at the drain end, a consistent carrier density is established in the channel. However, when V_{DS} is applied, the channel acts more like a variable resistor, showing a rise in potential from source to drain [2]. Although the charge transport mechanics of organic transistors differ from those of MOSFETs, the current-voltage characteristics from the linear to the saturation regime can be represented similarly. The source-to-drain current is regulated by the gate electrode. A charge accumulation layer forms at the OSC/insulator interface upon application of the gate voltage V_{GS}, and at this point, no current will flow across the channel until the V_{DS} is maintained at zero. A charge-gradient distribution arises and an I_{DS} flow across the channel between S and D when the low $V_{DS} < (V_{GS} - V_T)$ are applied. However, a saturation region and the I_{DS} can be obtained if V_{DS} is maintained greater than $(V_{GS} - V_T)$ beyond the pinch-off voltage, as shown in Figure 2, the drain current I_D exhibits feature of saturation and becomes almost constant [3]. For p/n type OSCs, an OTFT functions fundamentally like a capacitor, creating an electric field in the dielectric at negative/positive V_{GS}.

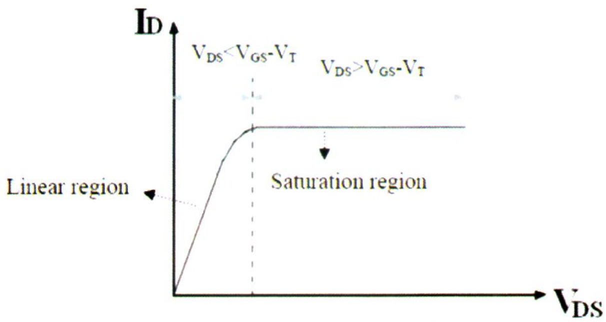


Figure 2. OTFT operation regions

Contact resistance between drain and source, R_c is represented by equation (1).

$$R_c = \rho\left(\frac{L}{Wd}\right) \quad (1)$$

where ρ is conductivity, L is the channel length, W is the channel width, and d is dielectric thickness.

R_{ON}, in the linear regimes is expressed in equation (2), where μ is carrier mobility, C_i is the capacitance of the gate dielectric and V_G is the gate voltage.

$$R_{ON} = \left(\frac{L}{W \mu C_i (V_G - V_T)} \right) + R_C \tag{2}$$

On the other hand, C_i is mathematically represented by equation (3).

$$C_i = \left(\frac{\varepsilon_r \varepsilon_0}{d} \right) \tag{3}$$

where ε_r is relative permittivity of material and ε_0 is permittivity of free space. In BGBC configuration, access resistance plays no role owing to alignment of the contacts and conducting channel on the same plane. However, bottom contact devices exhibit large contact resistance due to very small effective area for charge injection into the conducting channel as depicted in Figure 1. As semiconductor is deposited on two different materials such as gate dielectric and source/drain contacts simultaneously, this causes differences in surface energy and surface roughness between metal electrodes and insulator layer and force the OSC film to adapt different microstructures in two regions, which results in disordered regions in organic thin film, particularly near the source/drain contacts [4].

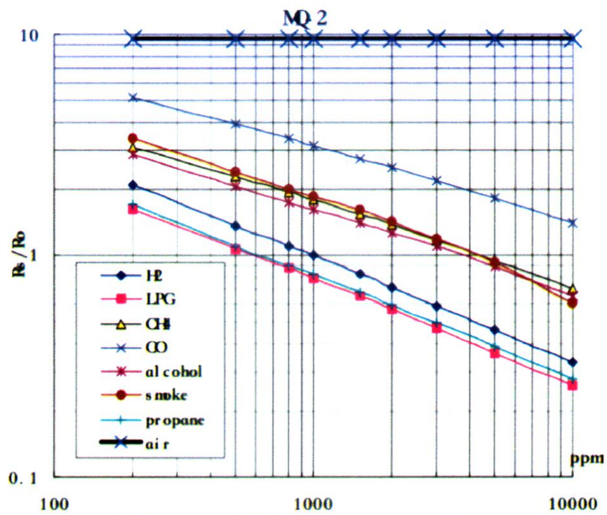


Figure 3. Benchmark MQ2 gas sensor performance [5]

Electric potential, E is created by the applied voltage across dielectric, influencing the behavior of the charge carriers in the organic semiconductor layer, which in turn ultimately controls OTFT's performance. Equation (4) expresses the relationship between E across the dielectric layer, and voltage applied to the transistor's gate electrode, V.

$$E = \frac{V}{d} \tag{4}$$

The ideal current-voltage relationship in the linear region is shown in equation (5).

$$I_D = \left(\frac{W}{L} \right) \mu C_i (V_G - V_T) V_D \tag{5}$$

where I_D is the drain current and V_D is the drain voltage.

The on/off ratio, $I_{ON/OFF}$ is the ratio between the currents flowing during accumulation and depletion. Depending on the channel conductivity, σ_s and thickness of active layer, χ_S, the on/off current ratio can be described in equation (6) for a device that is switching from cut-off to saturation.

$$I_{ON/OFF} = \frac{\mu C_i (V_G - V_T)^2}{\sigma_S \chi_S V_D} \quad (6)$$

Electronic sensors like the MQ2 gas sensor are used to measure the levels of gases in the atmosphere, including carbon monoxide, alcohol, smoke, methane, and LPG [5]. MQ2 is a metal oxide semiconductor. When the sensing component comes into touch with the gas, the resistance of the component changes. The detection of different gasses at different concentration is shown in Figure 3. The trend of this plot is used as a benchmark to validate the performance of BGBC OTFT developed in this work for CO_2 detection.

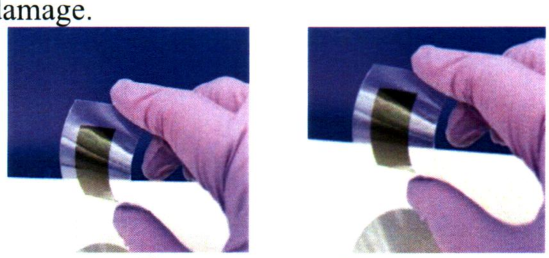
Due to the carbon-carbon triple bonds, the TIPS pentacene's bulky side group is forced away from the backbones, resulting in face-to-face interaction π–π stacking. When compared to pentacene, the π–π stacking of TIPS pentacene molecules significantly improves charge transport [6]. The fabrication method is important because it affects mobility values. For instance, hole mobility of 1.3 cm^2/Vs from TIPS pentacene spherulites due to the large grain size and crystal perfection in study of the crystallization modes of TIPS pentacene by adjusting the spin coating duration [7]. Next, highly orientated TIPS pentacene crystal growth technique using a blade coating yields crystals with a mobility of 1.74 cm^2/Vs [8]. When the polar and dispersive components of surface energy matched those of the semiconductor, the dielectric surface was finally adjusted, and TIPS pentacene microwires recorded a mobility of 2.26 cm^2/Vs [9]. These mechanisms greatly influence OTFT performance as sensor. Sensor sensitivity, *S* is represented by equation (7).

$$S = \frac{R_0 - R_S}{\Delta ppm} \quad (7)$$

where S is sensitivity in Ω/ppm, and Δppm is change in ppm value, R_0 is initial resistance without any gas supply and R_S is the measured resistance in the presence of CO_2. The sensing resistance under the presence of target gas is plotted in logarithmic graph. While in clean air, R_0 represents the sensory resistance. Based on Figure 3, as concentration of gas increases in ppm, R_S decreases and lead to decrease of R_S / R_0.

Methodology

PEDOT: PSS, is dispersed in Dimethyl Sulfoxide (DMSO) in a ratio of 4:1 by magnetic stirring at 300 rpm for 30 minutes at room temperature. Next the solution is deposited onto flexible Polyethylene Terephthalate (PET) substrate via screen printing technique. The sample is then left to dry at room temperature for a day to produce a flexible gate electrode as shown in Figure 4 (a). Next 5 grams of PVA is dissolve in 100 ml of deionized water by stirring at 300 rpm for 30 minutes to produce well dispersed dielectric solution. 1 ml of clear PVA solution is used in screen printing dielectric layer on gate electrode. The prepared sample is then left to dry at room temperature and is shown in Figure 4 (b). As seen in Figure 4, both layers fabricated via screen printing are able to withstand bending without damage.



(a) (b)

Figure 4: Fabricated flexible BGBC OTFT layers. (a) Gate electrode (b) PVA dielectric

Next, for drain and source electrodes, 20 wt % Al solution and toluene solution is prepared by ultrasonication for 30 minutes. TIPS pentacene, as semiconductive layer was purchased from Ossila. 15 mg of TIPS pentacene is stirred in 1 ml toluene at 300 rpm for 24 hours [10]. Drain and source are fabricated on PVA, whereas TIPS pentacene is fabricated on the electrodes via screen printing technique. The fabricated BGBC electrode is shown in Figure 5.

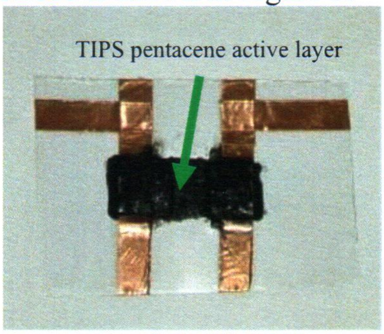


Figure 5. BGBC OTFT

Images of each layer fabricated via screen printing, which were obtained by using electronic microscope are also evaluated to analyse correlation between surface roughness and conductivity of BGBC configuration. Suitability and applicability of the fabricated materials in BGBC configuration in the detection of CO_2 is further tested by using the setup shown in Figure 6. Previous works reported that sample thickness prepared via screen printing is in μm range [11], whereas practical OTFT thickness is within nm range. However, more advanced techniques to fabricate nano-electronics such as photolithography are very costly and require proper setup conditions and is not possibly used in current lab scale setup. Therefore, screen printing is implemented in this works, whereas other advanced techniques will be potentially considered for future developments. CO_2 detection takes place in an acrylic gas chamber shown in Figure 6, which prototype a closed room. CO_2 detection by using OTFT is measured via resistance measurement obtained by using a multimeter. The change of resistance from starting, R_0 and final, R_S is measured at room temperature. Then, CO_2 is released at a constant flow rate. Resistance values are recorded as CO_2 concentration (in ppm) increases. After saturation, CO_2 flow into the acrylic chamber is terminated and is slowly released out. The response plot of fabricated CO_2 gas is then further evaluated.

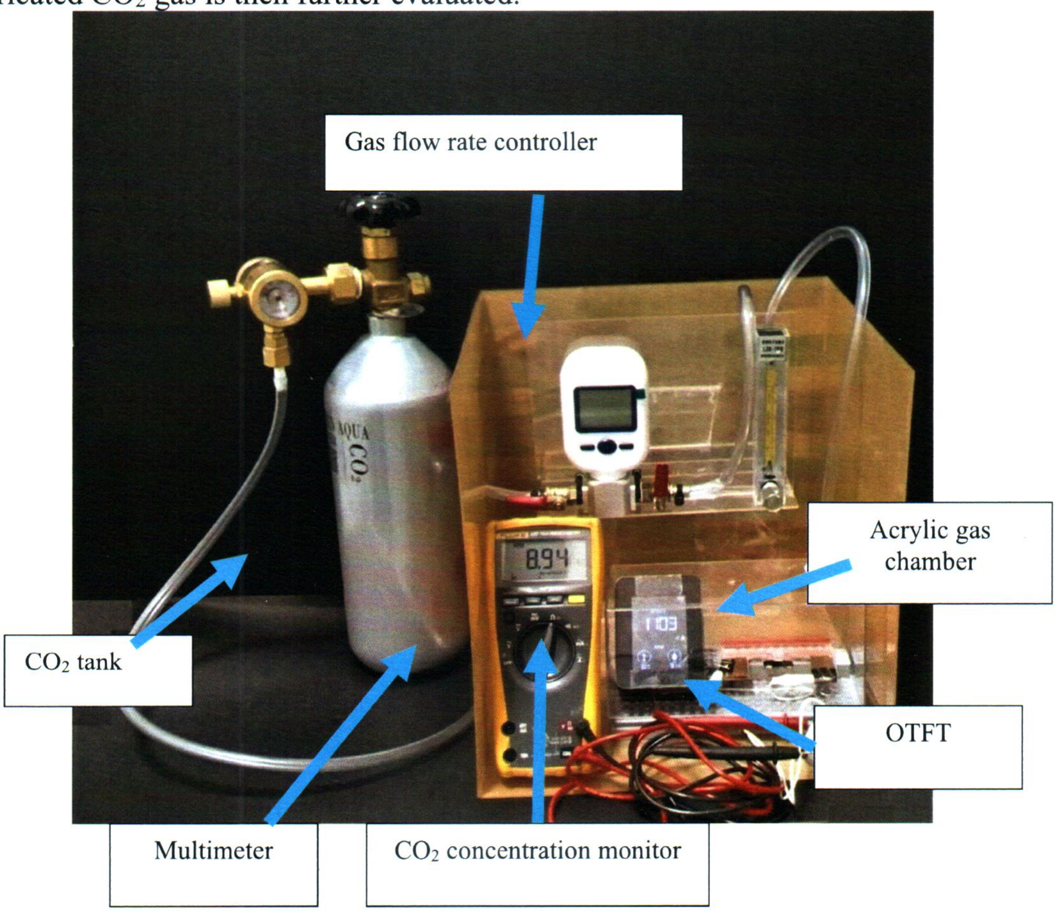


Figure 6. BGBC implementation in CO_2 detection

Results and Discussions

Every layer of BGBC OTFT is fabricated by using screen printing technique. Image analysis is conducted in MATLAB to verify proper surface roughness resulted from BGBC fabrication, to allow good adhesion of CO_2 molecules on sensor surface area. Pixel analysis conducted on gate, dielectric and source electrodes surface are shown in Figure 7. Histogram of PEDOT: PSS gate electrode Figure 7 (a) ranges towards darker ranges in the x-axis which peaks around 60. PEDOT: PSS solution is dark blue in colour, hence pixel distribution within darker range indicates that the solution has uniformly coat flexible PET substrate. PVA dielectric solution is transparent in colour, therefore in Figure 7 (b), there is no obvious difference in observed image and pixel distribution can also be seen in the dark pixel range. On the other hand, Al which is light grey in colour shows different pixel distribution towards lighter pixel range as seen in Figure 7 (c). Based on the results, it can be concluded that the deposition technique used in this work (screen printing technique) is suitable to be used as the prepared material solutions are uniformly deposited onto the designated surface area. These results are in good agreement with [11] where the darker area of the image pixel shows an almost constant and uniform distribution. Darker pixel analysis indicates that the darker tones or colours are distributed uniformly throughout the image. A more uniform appearance in the darker range may result from the coat or surfaces represented in the image having smooth textures or low surface roughness [12]. A homogeneous coat is produced because smooth surfaces tend to reflect light more uniformly.

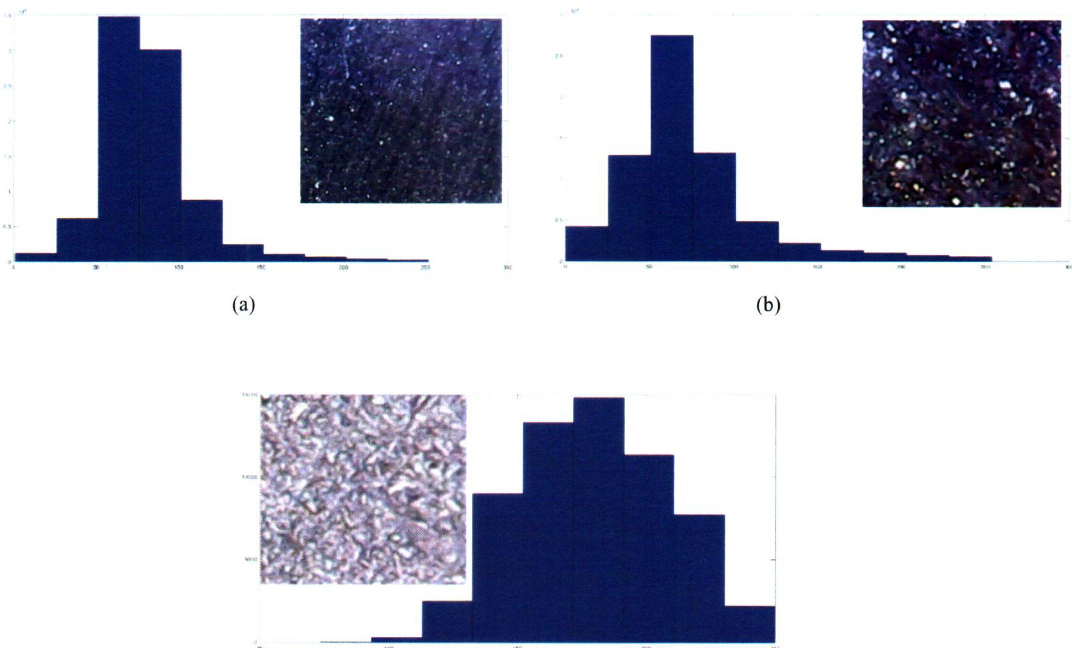


Figure 7. Pixel histogram of screen printed OTFT layers. (a) PEDOT: PSS gate (b) PVA dielectric (c) Al drain source layer

Coating layer thickness is measured by using a thickness gauge as shown in Figure 8. As seen in Figure 8 (a), gate electrode and PET substrate thickness is 170 μm, whereas PVA coated gate electrode thickness is measured at 177 μm as in Figure 8 (b). The difference between these two values is dielectric thickness of 7 μm. These results indicate that the implemented screen printing technique possibly produces coating thickness in μm range. Besides, thin dielectric thickness in BGBC thin film permits better charge transport. The gate bias, which causes polarization in the dielectric layer, can be used to vary the charge flow across the semiconducting channel between the source and drain electrodes. In a thin film structure, a thin dielectric layer decreases the distance between conducting layers. This closer proximity makes it simpler for charges to move between the conducting layers and improves conductivity [13]. As a result, surface energy matching between the semiconducting and dielectric layers is good, with low power consumption.

(a) (b)

Figure 8. Thickness measurement on flexible substrate. (a) PEDOT: PSS on PET (b) PVA on PEDOT: PSS coated PET

Performance of an OTFT gas sensor is influenced by electrical characteristics of the organic material, which in turn can be impacted by the presence of gas molecules. For instance, gas molecules can influence the conductivity, mobility, and density of charge carriers of organic materials. Electrical current flowing through the device changes due to this interaction. The change in electrical current is also correlated to resistance changes, according to Ohm's Law. Resistance change is monitored to detect the gas presence, representing reactivity of gas molecules on OTFT top structure. As CO_2 gas is supplied into the chamber at flow rate of 10 ml/minute, contact resistance is measured, and R_S / R_0 ratio is then plotted at different concentration as illustrated in Figure 9. In the measurement, the initial ambient CO_2 reading, R_0 was first recorded, indicating the condition with no CO_2 supply. Initially CO_2 reading was 1618 ppm and R_0 was 15 kΩ. CO_2 concentration of less than 1000 ppm, are generally referred to as safe level for indoor environment. Therefore, in this work, OTFT performance in CO_2 detection is evaluated within 1618 ppm to 5000 ppm, as prolong exposure above this value is considered dangerous. Later at CO_2 flow rate of 10 ml/min, resistance value increases with increasing CO_2 content. At 5000 ppm, R_S was 8 kΩ. Based on equation 7, sensitivity of OTFT gas sensor is 2.069 Ω/ppm. The plot in Figure 9 shows decreasing trend. As gas concentration increased, R_S decreases. Thus, R_S / R_0 ratio consequently decreases too. The attained plot pattern shows the same decreasing trend as benchmark commercial MQ2 gas sensor response previously shown in Figure 3, indicating that the developed BGBC OTFT in this work is comparatively reliable as gas sensor.

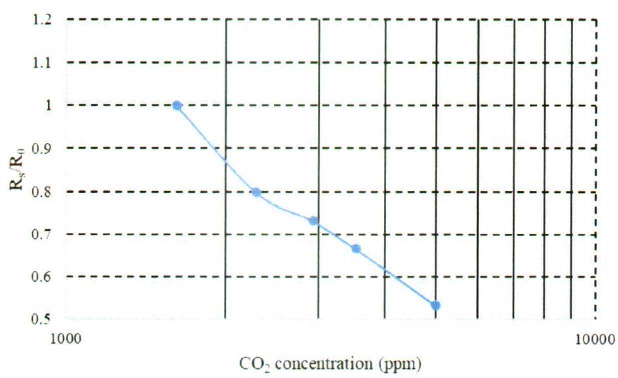


Figure 9. Sensor response with increasing CO_2 concentration

Conclusion

In low drain voltage operating region (linear regime) of conventional OTFT, contact resistance is one of the factors affecting output characteristics. In this work, PEDOT: PSS is fabricated as the gate, PVA is the dielectric, Al is used as drain and source electrodes, and TIPS pentacene is the active semiconductive layer. Selected materials which are developed in BGBC configuration are experimentally tested in closed room prototype and have successfully demonstrated CO_2 detection with sensitivity of 2.069 Ω/ppm. In future works, this work will be proceeded for fabrication by using more advanced nanoscale technique, and will be further analysed. In addition, the sensor can be possibly tested to detect other types of gasses such ammonia, hydrogen and many others. Hence, the studied BGBC OTFT configuration is indeed significant to find application in the field of nanoscale gas sensor.

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