

Phthalocyanine Organic Thin-Film Transistors for the Detection of dimethyl methyl phosphonate (DMMP)

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Abstract:

The electrical properties of Metal-Phthalocyanines (M-Pc) are affected upon exposure to gases containing not only some oxidizing/deoxidizing molecules but also nerve agent simulants. This phenomenon finds application in the use of Organic Thin-Film Transistors (OTFTs) based on copper phthalocyanine (CuPc) and cobalt phthalocyanine (CoPc) as gas sensors. In this work, tests of dimethyl methyl phosphonate (DMMP) detecting were carried out, and the sensing mechanism of OTFT DMMP sensors was further investigated by the transfer curve of OTFTs and the UV-Vis absorption spectra of sensitive films before and during DMMP vapor exposure. The results showed that M-Pc-based OTFTs can represent a new class of DMMP sensors.

Key words: OTFTs, CuPc, CoPc, gas sensors and DMMP

Introduction

The use of chemical weapons against civilians by terrorist groups or fanatic individuals is not just horror fiction anymore, but an absolute real threat [1]. The fast and accurate detection of chemical warfare agents (CWAs) is essential to protect human beings, thus many researchers have already attempted to detect toxic gases using various kinds of sensors. Among them, organic thin-film transistors (OTFTs) offer a great deal of promise for application in chemical and biological sensing [2]. For the detection of CWAs, there is a demand for small, portable, and inexpensive sensors. OTFTs have many advantages over other types of sensors that may allow them to meet these needs, such as their ease of deposition, ability to operate at room temperature and the multi-dimensional pattern [3-4]. Therefore, there has been an increasing progress in OTFT performances during the last decade.

Metal-Phthalocyanine (M-Pc) is known to be very sensitive and also selective to different gases and solvents as an account of the central metal atoms of the molecule, which can be easily varied. Phthalocyanine especially, due to their highly thermal stability, possesses a wide range of chemical and physical properties, that make them interesting as an active layer in OTFTs [3]. Over the past decade, the use of M-Pc as a sensitive component has been

investigated for many kinds of gases [5-6]. However, to the best of our knowledge, there were few reports for the DMMP sensor using the M-Pc as the sensitive materials. R. D. Yang and J. Park had developed a pulsed gating method to enhance the baseline stability of OTFT chemical sensors based on the M-Pc, and the analytes employed were methanol, DIMP and DMMP [7].

This paper describes the preparation of a gas sensor based on OTFTs obtained from vacuum-deposition copper phthalocyanine (CuPc) and cobalt phthalocyanine (CoPc) on a thermally grown SiO₂/Si wafer. The saturation current of OTFTs was used as a good parameter for monitoring the dimethyl methyl phosphonate (DMMP) gas, the simulant of nerve agents, and the gas-sensing mechanism of OTFTs was further investigated.

Experimental

The OTFT was fabricated using standard semiconductor processing techniques. The channel length and width is 10 and 4000 μm, respectively. The insulating layers SiO₂ is 195 nm in thickness. Titanium (Ti) (20nm) and gold (Au) (50nm) bilayer was sputtered on top of the gate dielectric layer as the source and drain electrodes. The CuPc and CoPc were purchased (purity>99.5%) and used without any purification, which was deposited by vacuum deposition at a average deposition rate of 0.3

Å/s. The substrate temperature was maintained at 260 °C, and the thickness of the active layer is about 90 nm.

The layout of an OTFT sensing experiment was shown in Fig.1, illustrating the delivery of DMMP molecules from the sample reservoir to the surface of the OTFT gas sensor. 100 ppm standard DMMP gases were obtained, and the gas concentration is controlled by the mass flow controls. The source-drain voltage and the gate voltage were both swept between 0 and -60 V. The saturation source-drain currents were recorded as the output signals of sensors using a Keithley 4200-SCS source measurement unit at room temperature.

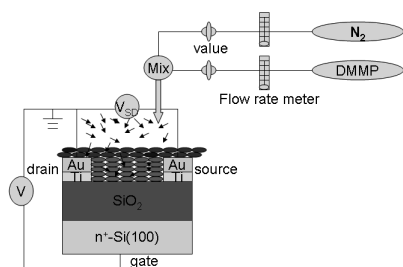
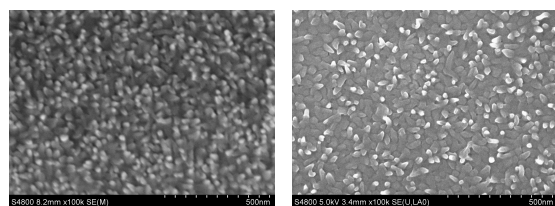


Fig. 1. Schematic system of DMMP delivery with OTFT under experiment

The UV-vis absorption spectra of phthalocyanine thin films were recorded on a Shimadzu UV1700 spectrometer using an uncoated glass as the reference. The surface morphology was assessed with a Hitachi S4800 scanning electronic microscope (SEM).

Microstructure Characterization

It is well-known that the surface morphologies and the grain boundaries of organic thin films can influence the sensing property of OTFT sensors [8]. Fig. 2 shows the SEM images of CuPc (a) and CoPc (b) thin films, which both indicates the plate-like structures, with the topmost layer of plates standing perpendicular to the surface. For the gas sensor application, surface structures like this film are desired because of the large surface area and more adsorption sites compared to films with large bulk grains.



(a) CuPc

(b) CoPc

Fig. 2. The SEM images of M-Pc thin films

Current voltage characteristics of OTFT

The I_d - V_d characteristics of CuPc and CoPc OTFT sensors are shown in Fig.3, which exhibited the obvious linear and saturation regions. It was noticeable that the source-drain current of CuPc OTFT sensor was apparently larger than that of CoPc OTFT sensor. It was because that the nature of the sequestered metal ions has an influence on the physicochemical properties of the M-Pc. And the results indicated that the conductivity of the CuPc thin film was superior to that of CoPc film. For the sensor application, it is more desirable to have a higher source-drain current, so that the CoPc OTFT was not very suitable for the DMMP sensor compared with CuPc OTFT in this sense.

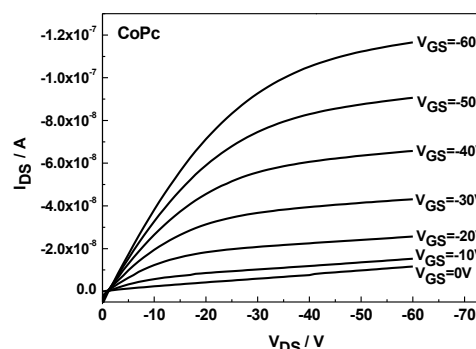
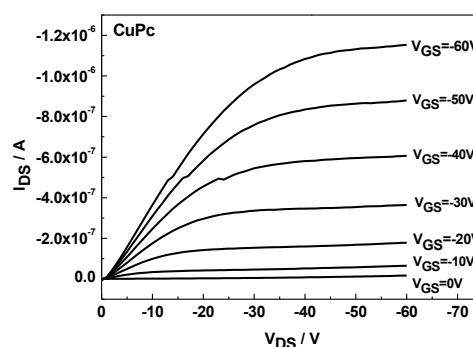


Fig. 3. I_d - V_d characteristics of CuPc and CoPc OTFT sensors

Performance of OTFT sensors

Fig.4 showed the changes in drain-source current as a function of time when the CuPc and CoPc OTFT sensors were exposed to different exposure/evacuation cycles of DMMP gases in concentrations ranging from 40 to 80 ppm at room temperature. The measurements of the time dependence of the drain-source current in the OTFT sensors were made at a gate voltage of -40V and a drain-source voltage of -50V. As can be seen in Fig.4, the drain-source current decreased rapidly whereas it could not recover completely to its original baseline. The results also indicated that the conductivity and the

response of the CuPc thin film were all superior to those of the CoPc film.

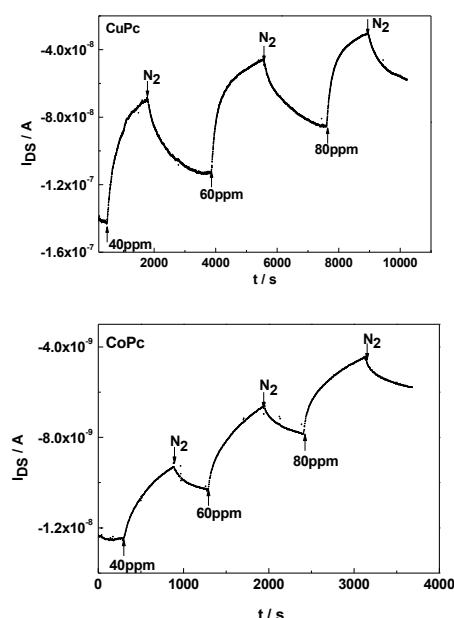


Fig. 4. Response transients of the prepared OTFT sensors to DMMP

Sensing mechanism

Fig. 5 plotted the square root of the saturation drain current of CuPc and CoPc OTFT sensors versus gate voltage before and during 50 ppm DMMP gas exposure.

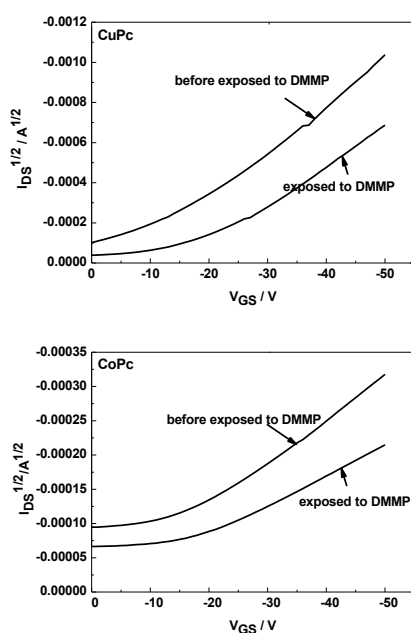


Fig. 5. Square root of the saturation drain current of CuPc and CoPc OTFT sensors versus gate voltage before and during DMMP gas exposure

It was remarkable that the source-drain current was not zero at zero gate bias, which was because that thermally evaporated organic thin films are unintentionally p or n doped and only

highly pure materials originate TFTs that are off already at zero gate bias.

The threshold-voltage (V_T) was extracted from the measured drain current versus gate voltage transfer characteristics by the linear extrapolation, and the changes of the threshold-voltage (ΔV_T) of CuPc and CoPc OTFT sensors were shown in Tab. 1 and Tab. 2, respectively. It can be seen that the V_T value shifted further toward the negative direction in comparison to the V_T of standard OTFT sensors without exposure to DMMP gas. Since the shift in V_T can be estimated according to Poisson's equation [15]:

$$\Delta V_T = \frac{-N\mu_l}{\epsilon} \quad (1)$$

Where N is the density of the adsorption site, μ_l is the number of dipole moments, and ϵ is the permittivity of the organic layer. Therefore, the ΔV_T may be ascribed to the interactions between the dipolar molecules adsorbed on the active layer or adsorption sites between grain boundaries of the Pc thin films, and was related to the change of the work function at the interface between the organic semiconductor layer and the insulator, induced by the adsorption of the polar molecules. The variations in the field-effect mobility ($\Delta\mu_{\text{sat}}$) of OTFT sensors with and without exposure to DMMP (50 ppm) are also summarized in Tab. 1 and Tab.2, which indicated that the μ_{sat} values decreased when OTFT sensors were exposed to DMMP compared with those not exposed to the gas.

Tab. 1: The values for CuPc OTFT parameters such as V_T and μ_{sat} as functions of DMMP gases

	CuPc (no DMMP)	CuPc (50ppm DMMP)
$V_T(\text{V})$	-9	-16
$\mu_{\text{sat}}(\text{cm}^2/\text{V}\cdot\text{s})$	-1.16×10^{-4}	-0.44×10^{-4}
$\Delta V_T(\text{V})$	-7	
$\Delta\mu_{\text{sat}}(\text{cm}^2/\text{V}\cdot\text{s})$	0.72×10^{-4}	

Tab. 2: The values for CoPc OTFT parameters such as V_T and μ_{sat} as functions of DMMP gases

	CoPc (no DMMP)	CoPc (50ppm DMMP)
$V_T(\text{V})$	-2.0	-3.5
$\mu_{\text{sat}}(\text{cm}^2/\text{V}\cdot\text{s})$	-1.15×10^{-5}	-0.53×10^{-5}
$\Delta V_T(\text{V})$	-1.5	
$\Delta\mu_{\text{sat}}(\text{cm}^2/\text{V}\cdot\text{s})$	-0.62×10^{-5}	

It was believed that the change of saturation drain current can be attributed to the variation of both threshold voltage and field effect mobility [8], hence the changes of these two parameters are consistent with those of drain currents.

Fig. 6 displays the UV-vis absorption spectra of CoPc and CuPc thin films before and during DMMP gas exposure. The CuPc thin film shows the bands at about 615 nm and 690 nm and the CoPc thin film shows the bands at about 610 nm and 680 nm, which should be due to the $n-\pi^*$ transition. From the plots shown in Fig.6, it can be noted that there was no new absorption band appeared, and the exposure to DMMP only resulted in the change of the absorption values, indicating a physical absorption, probably a weak electrostatic force of the van der Waals type in the active film, and no chemical interaction or the structural change occurred. Therefore, the change in currents observed when OTFT sensors were exposed to DMMP should be a combination of effects on charge carrier mobility and threshold voltage based on the above measurement and analysis.

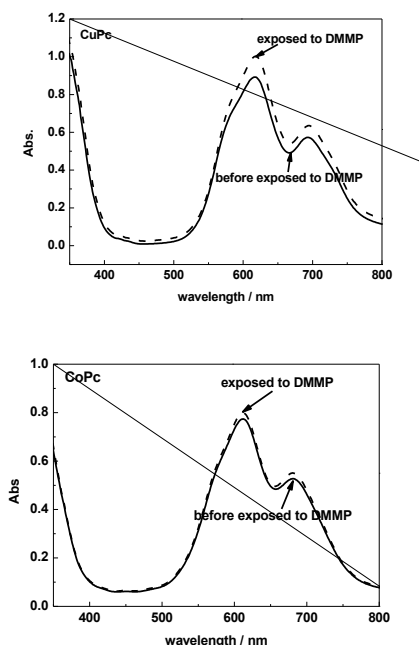


Fig. 6. UV-Vis absorption spectra of CuPc and CoPc thin films before and during DMMP gas exposure

Conclusion

The DMMP sensors had been prepared based on OTFTs made from vacuum deposited CuPc and CoPc thin films on thermally grown SiO_2/Si wafers. The time dependence of the drain-source current had been observed when exposed to DMMP gases ranging from 40-80 ppm, which showed that the response characteristics of CuPc OTFT sensors were superior to those of CoPc OTFT sensors. Also,

the response characteristics of the OTFT DMMP sensors had shown results in the threshold-voltages being shifted and a decrease in the field-effect mobility, and no chemical interaction or the structural change occurred by the UV-vis absorption spectra testing. Therefore, the change in currents should be a combination of effects on charge carrier mobility and threshold voltage.

Acknowledgements

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