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Oxidizing gas sensing properties of mesogenic copper octakisalkylthiophthalocyanine chemoresistive sensors

N. Kılınç [a], D. Atilla [b], S. Öztürk [a], A.G. Gürek [b], Z.Z. Öztürk [a,c,*], Vefa Ahsen [b,c]

[a] *Gebze Institute of Technology, Faculty of Science Department of Physics, 41400 Gebze-Kocaeli, Turkey*
[b] *Gebze Institute of Technology, Faculty of Science Department of Chemistry, 41400 Gebze-Kocaeli, Turkey*
[c] *TÜBİTAK-Marmara Research Center, Materials Institute, 41470 Gebze-Kocaeli, Turkey*

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ABSTRACT

In this study, the effect of oxidizing gases, such as oxygen (O_2), nitrogen dioxide (NO_2), and ozone (O_3), on a liquid-crystalline copper octakisalkylthiophthalocyanine[$(C_6S)_8$PcCu] thin film was investigated in the temperature range of 25–150 °C. Starting from a chloroform solution of $(C_6S)_8$PcCu, a jet-spray technique in an inert ambient atmosphere was used to coat the thin film of the compound on to an Interdigital Transducer (IDT) with gold electrodes. The concentration ranges for NO_2 and O_3 exposed to the $(C_6S)_8$PcCu thin film were 1–10 ppm and 50 ppb–50 ppm, respectively. The response time in NO_2 measurements was observed to be approximately 1 min at room temperature, and it decreased to a few seconds with increasing temperature. A good sensor response of 2000% ppm^{-1} was observed when the sensor was exposed to 1 ppm NO_2 at room temperature. The oxidizing gases were found to be desorbed by annealing the thin film.

1. Introduction

It is possible to place around seventy different elemental ions in the central cavity of phthalocyanines, and the choice of central metal cation can strongly influence its physical properties. Metallophthalocyanines (MPcs) have been extensively studied in the area of gas sensors, liquid crystals, organic semiconductors, and field effect transistors [1–5]. MPcs have exhibited high sensitivity towards weak concentrations of oxidizing and reducing gases such as nitrogen dioxide (NO_2), ozone (O_3), chlorine, and bromine [6–8], and potentialities to detect even volatile organic compounds [9,10]. The great reactivity of phthalocyanines towards oxidizing species induced many studies on sensors using these molecular semiconductors as sensitive elements.

Copper (II) phthalocyanines (CuPcs) have attracted much attention because of their potential applications in chemical sensors [11]. The films of MPcs that show mesomorphic properties at room temperature have been used as photoconductors and gas sensors in molecular electronic devices. The ordered MPc films that are obtained from liquid crystalline MPc compounds are more sensitive than disordered MPc films [12–14]. Many experimental results have demonstrated that the mesogenic phthalocyanine can adopt a high vertically ordered composition as well as high charge-carrier mobility [15]. This is undoubtedly beneficial for the further improvement of the performance of the CuPc based gas sensor devices.

The mesogenity of MPc was first demonstrated in alkoxymethyl-substituted CuPc in 1982 [16]. Since then, CuPcs with liquid-crystalline properties have been synthesized with different types of substituent. The most common ones are alkyl, alkoxy or alkoxymethyl chains [17–19]. The liquid-crystalline properties of octa-alkylthio-substituted Copper (II) phthalocyanine derivatives [$(C_nS)_8$PcCu] with n = 6, 8, 10, 12, 16 have also been investigated [20,21]. It has been shown that alkylthio-substituted phthalocyanines [$(C_nS)_8PcH_2$], and the copper complexes $(C_nS)_8$PcCu display higher conductivities than their alkoxy-substituted phthalocyanines in their mesophase [20]. The mesogenic properties of $(C_6S)_8$PcCu were studied by differential scanning calorimetry, X-ray diffraction, and optical microscopy. These phthalocyanines form the columnar hexagonal mesophase over a wide temperature range [21b].

The goals of the present work are (i) to investigate oxidizing gases such as O_2, NO_2 and O_3 sensing properties of the $(C_6S)_8$PcCu thin film, and (ii) to explain the different sensing behavior of liquid-crystalline copper octakisalkylthiophthalocyanine [$(C_6S)_8$PcCu] thin film for O_2, NO_2 and O_3 gases.

2. Experimental

For the chemoresistive sensor measurements, the $(C_6S)_8$PcCu compound was coated from a solution of the compound in chloroform onto photolithographically patterned Interdigital Transducer (IDTs) using a home made air brush system in an inert ambient atmosphere. These IDTs consisted of 10 interdigital pairs of gold fingers on a glass

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[*] Corresponding author. Gebze Institute of Technology, Faculty of Science Department of Physics, 41400 Gebze-Kocaeli, Turkey. Tel.: +90 2626051306; fax: +90 262 6538490.

E-mail address: zozturk@gyte.edu.tr (Z.Z. Öztürk).

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Table 1
Phase transition temperatures and enthalpy changes for the $(C_6S)_8PcCu$ determined by DSC (heating and cooling rates are 10 °C·min^{-1}, heating range is from − 10 to 300 °C) [21b].

Compound	Phase $\xrightarrow{T/°C[\Delta H(kJ\cdot mol^{-1})]}$ Phase
1	$K \underset{-1[12.11]}{\overset{8[21.73]}{\rightleftharpoons}} D_h \xrightarrow{ca.300} dec.$

substrate, with the thickness of 120 nm, the width of 100 µm, and the spacing of 100 µm between adjacent fingers. The overlapping length of the IDTs was 5 mm. The thickness of the films, which was determined by a surface profilometer (Veeco, Dektak 6), was approximately 200 nm. For IDT, gold was selected as the electrode material, deposited in the comb configuration onto the active layer, since it is well-known that it forms ohmic contact to phthalocyanine. The samples were placed in a home made measurement cell of a volume of 1 L through which a gas could be passed. The measurement cell consists of stainless steel. The gas concentration was varied by using a MKS Instruments mass flow controller, model 647. The dc currents of various samples were monitored by an electrometer, Keithley model 6517A Electrometer/ High Resistance Meter. The temperature control was carried out by a Lakeshore 340 temperature controller while a platinum thermometer measured the temperature of the sample, and a 60 ohm heating resistor was placed under the sample. The working parameters, such as the operating temperature, gas flow rates, and current through the samples were controlled by a personal computer with an IEEE 488 board.

The experimental procedure was performed by heating the sensors to 150 °C and waiting for 10 min at this temperature under the high purity N_2 flow in order to obtain ordered films and the desorption of the absorbed oxidizing gases. A constant bias voltage of 1 V was applied to the $(C_6S)_8PcCu$ thin film sensor and the dc current was measured until a steady current reading had been obtained. The dc current (sensor responses) was monitored continuously under high purity N_2 flow (flow rate: 500 sccm) to establish the baseline of the device, and was recorded using an IEEE 488 data acquisition system that is incorporated to a personal computer. Then an active gas was admitted in its desired concentration mixed with high purity N_2, and the current was recorded during a period of time necessary to obtain saturation current and calculate the response time of the sensor. The active gas was then turned off, and the sample was left to recover in high purity N_2 flux. The returning of the current to its initial value confirms the reversibility of the process. All oxidizing gas sensing measurements were obtained in the temperature range of 25–150 °C, where the $(C_6S)_8PcCu$ is in liquid-crystalline phase.

The mesogenic properties of the compound were described in a previous work [21b]. Phase transition temperatures and enthalpy changes, which were established by DSC and polarizing microscopic observations for the $(C_6S)_8PcCu$ compound, are listed in Table 1. The compound has only one type of mesophase and forms a columnar hexagonal mesophase over a wide temperature range from 8 to 300 °C [21b]. To investigate O_2 doping effect, the high purity dry air (21% O_2) was used as O_2 source, and 500 sccm high purity dry air flux was flown for 1 h until the electric current reached a steady state value. Then, the measurement cell was purged with 500 sccm high purity N_2 flow. For our measurements of NO_2 and O_3 sensing properties, the high purity N_2 stream flowed through the test chamber until the electric current reached a steady state value (defined as base line), and then the valves of the chamber were closed. NO_2 and O_3 gases with different concentrations were injected into the measurement cell through a septum with a gas tight micro syringe The concentration ranges that are exposed to the $(C_6S)_8PcCu$ thin film were 1–10 ppm for NO_2, and 50 ppb–50 ppm for O_3. For measurements of O_3 sensing properties, the 50 ppb O_3 was injected in to the measurement cell, and we waited for 300 s until the current reached a steady state value, and we increased the O_3 concentration to its next value every 300 s. After 50 ppm O_3 gas was injected into the measurement cell, the cell was cleaned with 500 sccm high purity N_2 flow.

3. Results and discussion

3.1. O_2 doping

In generally, oxidizing gases enhance the conductivity of MPcs, because they are p type semiconductors, and the number of charge carriers in them increases when the oxidizing gases are absorbed. Incomplete desorption of oxidizing gases, which may modify subsequent adsorption properties, originates from the strong bonding of the gas molecules to the surface. Before oxygen doping measurements, the $(C_6S)_8PcCu$ thin film is heated to 150 °C and kept for 10 min in this temperature with a heating and cooling rate of 1 °C/min in N_2 gas flow in order to allow the arrangement of our liquid crystal films and the desorption of oxidizing gases. Fig. 1 shows the current versus time for O_2 doping at room temperature and at 150 °C. It is clearly seen that the current increased, but did not reach the saturation value for an hour for both temperatures. We expect that it is required to wait a long time, maybe a month, to fully dope with O_2 at room temperature. Our results presented in Fig. 1a are in agreement with this expectation. The sensing characteristics of our sensor shown in Fig. 1a indicates that the initial base line dc current value is not recovered in an hour.

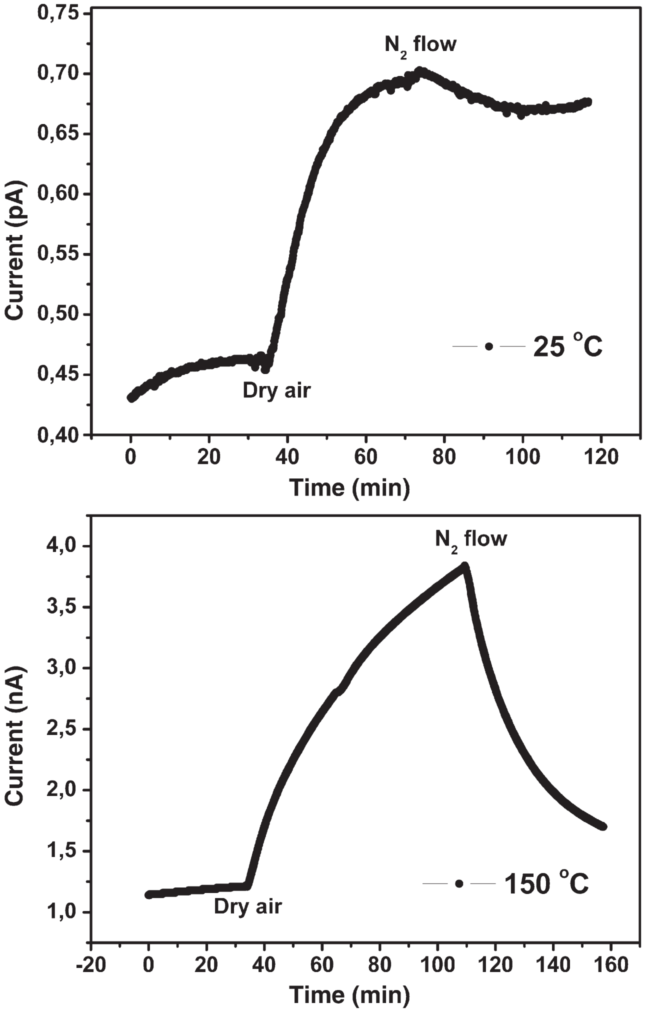

Fig. 1. The current versus time for O_2 sensing at room temperature, and at 150 °C.