Sensors and Actuators B 179 (2013) 54–60

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Nonconventional phthalocyanines for field effect gas detection

W. Simmendinger*, A. Oprea, N. Bârsan, U. Weimar

Institute of Physical and Theoretical Chemistry, auf der Morgenstelle 15, 72076 Tuebingen, Germany

ARTICLE INFO

Article history:
Received 12 July 2012
Received in revised form 1 October 2012
Accepted 11 October 2012
Available online 22 October 2012

Keywords:
Metal phthalocyanine
NO_2 sensing
Work function
Kelvin Probe

ABSTRACT

Metal (TiO and Zn) phthalocyanines that are not currently investigated for gas sensing applications have been deposited by thermal vacuum evaporation as thin layers and evaluated in operando Kelvin Probe setup as NO_2 sensing materials. From the raw data their calibration curves have been inferred and some sensing parameters determined. Comparative conductometric evaluations have also been performed. On the basis of the experimental information the main peculiarities of the gas responses have been identified and discussed.

1. Introduction

After their initial use as pigment or dye it was found that the metal phthalocyanines (MPcs) change their electrical properties under the sorption and desorption of oxidizing gases [1–4]. Therefore, the gas sensing community tried to utilize the MPcs as sensitive layer for e.g. NO_2-detection, where it is definitely need of monitoring due to its poisonous and carcinogenic properties. Nevertheless, up to now, there is no commercially available gas sensor based on MPcs on the market, although they offer several advantages, like cost effective production, low power consumption, thermal and chemical stability, etc. These features are seldom encountered at the already established NO_2 gas sensors, such as the metal oxide based ones, which unfortunately have reduced selectivity and, moreover, operate at rather high temperatures or at the more specific electrochemical cells that are expensive and have a limited lifetime.

The gas sensing characteristics of the MPcs depend on the nature of the central metallic atom [5,6], on the substituents at the organic ring and also on the crystalline structure of the material, which can be influenced by chemical/thermal pre-treatments [7–9]. Fine tuning of Pc's composition and morphology can result in films with increased gas sensitivity, optimized for different gas sensing application such as ambient surveillance, fire detection and diseases recognition [10,11]. Meanwhile NO_2 concentrations down to 10 ppb are experimentally measurable with MPc based field effect sensors [11].

The interaction between the MPcs and the analytes takes place in different ways with different strengths. It ranges from unspecific and weak dispersion interactions, (common to organic compounds) which causes small but fast changes in the layers properties (effect is mostly utilized in gravimetric measurements [12–15]), to strong interactions with oxidizing gases, leading to the formation of free charge carriers (usually holes) via charge transfer complexes [16–18]. The last process subsequently alters the electrical properties of the semiconducting MPcs (usually having a p-type conduction) resulting in a good sensitivity and fair selectivity.

For a successful implementation in practical applications some known drawbacks of the gas sensing with Pcs have to be, however, overcame. The main one is the long recovery time due to the strong interactions between MPcs and the oxidizing gases (addressed above). Also the long term stability of some MPc layers that depreciate after few weeks or even days has to be improved. In such cases, convenient application types and suited readout scenarios/algorithms might be required.

The MPcs gas sensors proposed in the literature are mainly chemoresistors [5,6] or field effect devices [10,11]. The field effect readout has several advantages:

- Uses signals produced by the sensing layer surface [19–21], which, in principle, should increase the specificity of the sensor gas response, eliminating the contribution of the dispersion interaction (significant for the volume effects based transducers like the gravimetric ones). Simultaneously, a certain decrease in the response and recovery times is expected because the diffusion times into and out of the sensing material are avoided.
- Very low power consumption, as in the case of any electrostatic readout.

* Corresponding author.
E-mail address: wolfram.simmendinger@ipc.uni-tuebingen.de (W. Simmendinger).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.10.064

- Easily incorporation in application specific integrated circuits (ASICs) with increased market potential.

The earliest and most investigated MPc is the CuPc [6]. Oxidizing gases (NO_2, O_3) and halogens (Cl) have been detected with conductometric (down to 10 ppb [22–24]) and work function (down to ~1 ppb [11,25]) sensors. With the time the number of available MPcs increased, stimulating the interest for related gas sensing devices (PbPc, NiPc, CoPc [5,6,26–30]).

However, there are several MPcs, whose suitability as gas sensing materials have been, until now, not very intensively investigated. For instance, only few conductivity [31,32] and no Kelvin Probe (KP) measurements gas exposure have been performed on titanylphthalocyanine (TiOPc), even though field effect measurements for organic electronics have been reported [33,34]. Actually, in [33] a comparison between the output transfer characteristics of an organic TiOPc field effect transistor in NO_2 atmosphere (20 ppm in N_2) and vacuum has been made. Therefore no/scarce information about the KP/work function response of the TiOPc to oxidizing gases like NO_2 is available. Also ZnPc lacks the data about KP gas effects in spite of the fact that it is since longer time in the attention of gas sensing research [6,35–39].

In this context seemed us useful to make some combined operando investigations on TiOPc and ZnPc films. The operando method [20,40] supposes the evaluation of the device or material samples under conditions similar to those being employed during the foreseen application. Thus KP, conductometric, gravimetric and infrared absorption measurements under controlled atmosphere with focus on the field effect applications/implementations have been performed. The gravimetric and infrared data are not reported here, the measurements being still in progress.

2. Experimental

2.1. Sample preparation

Because of their high thermal and chemical stability, but poor solubility the TiOPc and ZnPc layers have been deposited by vacuum thermal evaporation on appropriate substrates. The studied MPcs have been purchased from Sigma–Aldrich and purified before the deposition through a bake-out procedure up to 400 °C. For the KP samples 7 mm × 9 mm silicon substrates covered with a 800 nm Au/20 nm Ti electrodes have been produced (Ti layer improved the adhesion of the Au electrode to the Si). The dc- conductance samples required interdigitated transducers on sapphire substrates and having 50 μm line spacing and width. In a deposition batch have been included all types of substrates by using a dedicated holder and a common shadow mask. The process has been performed under 3×10^{-7} mbar, with a deposition rate of 0.02 nm/s at a temperature of 400–450 °C, resulting in ~100 nm MPc layers.

Since the substrates have not been intentionally heated, the amorphous phase of the TiOPc and the α-modification of the ZnPc have been obtained. Under a 24 h exposure to saturated ethanol vapour it was possible to transform the amorphous TiOPc-layer into its α-modification [41,42].

Finally the samples for the Kelvin Probe and dc-measurements have been mounted on heatable sockets in order to enable measurements at temperatures higher than the room one.

2.2. Sample characterization

The characterization of the samples has been made, as accounted for above, in an operando evaluation set-up, including a computer controlled gas mixing system and remote operated measurement instruments (Fig. 1). In order to enable their

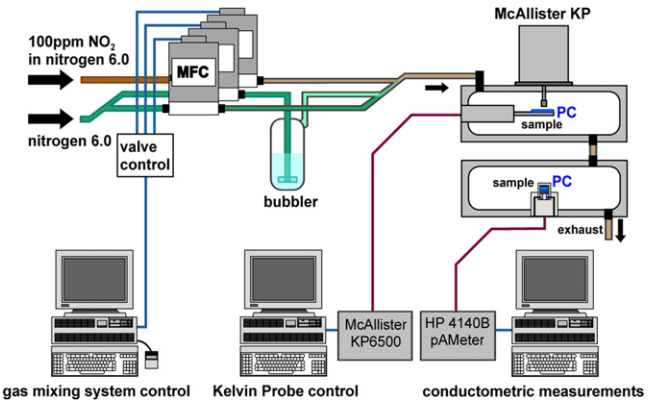

Fig. 1. Experimental setup, consisting of a gas mixing system, operando measuring chambers and investigation apparatus (McAllister Kelvin Probe and Hewlett Packard picoampermeter).

dynamic (continuous gas flow) gas exposure, the samples have been mounted into dedicated Teflon® (or Teflon® coated) measuring chambers. The main investigation tool was the non-locking KP 6500 from McAllister Technical Services. The results are reported as delivered by the apparatus, that is, as contact potential differences [CPD] [19,20]. To convert them to work function changes a multiplication with the electron charge (−e) has to be carried out. The conductometric measurements have been performed with the HP 4140B picoampere metre (pA-metre) and Keithley 617 programmable Electrometer. The chamber for the dc-measurements has been connected downstream to the KP measuring chamber, but no noticeable influence (under steady state conditions) of the exposure order was observed. This happens because the sensing mechanisms leading to the detection of oxidizing gases with phthalocyanines do not suppose the chemical conversion of the analyte to other compounds and the analyte concentration remains constant along the whole measurement chain. This would be not the case for other sensors, as, for example, the metal oxide chemo-resistors, where the reducing gases catalytically burn on the sensor surface, so that the downstream concentration of the analyte is smaller than the upstream one.

In all performed measurements (KP and conductometric) has been employed the gas exposure protocol presented in Fig. 2. 6.0 purity dry N_2 was the carrier gas in the first half of the exposure sequence (1; 3; 5 ppm NO_2). In the second half of the exposure sequence (with the same NO_2 concentration steps) 50% relative humidity (r.h.) background has been added to N_2 (through a high

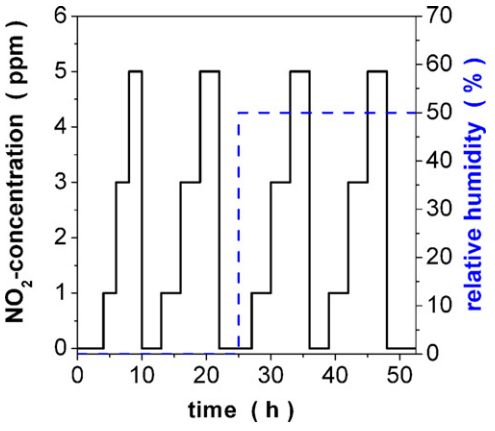

Fig. 2. Gas exposure protocol utilized for the KP and conductometric evaluation of TiOPc und ZnPc.