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Adsorption induced phase transition in Ti(Pc)$_2$ gas sensing films: A joint AFM-EDXR study

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HIGHLIGHTS

- The NO_x gas/$TiPc_2$ sensing film interaction is investigated in real time.
- Simultaneous EDXR/AFM techniques disclose a phase transition in the sensing material.
- An oscillating α to β_1 phase transition is induced by the presence of NO_x molecules.
- When the sensing process is concluded, the material turns to the most stable phase.

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ABSTRACT

The morphological properties of thin metal phthalocyanine films, used as active material in gas sensing devices, are studied. Morphological changes, such as bulk or surface phase transitions, are key phenomena, having a determinant influence on the final properties and stability of the materials and devices. In this work, we successfully prove that joint in-situ atomic force microscopy and Energy Dispersive X-ray Reflectivity can be used, not only to monitor the sensing activity of bi[phthalocyaninato(2-)]titanium(IV) films, but also as a powerful tool to disclose the physical-chemical process beneath the sensing activity. Indeed it is shown that NO_x adsorption activates a phase transition in the $TiPc_2$ film, characterized by an oscillating behavior between two metastable states. Such phenomena endure as long as the gas molecules are present, finally evolving into the thermodynamically most stable phase. Fourier transform infrared spectroscopy analysis supports the above conclusions.

1. Introduction

In developed and rapidly industrializing countries a major threat to clean air is posed by traffic emissions. Petrol- and diesel-engined motor vehicles emit a wide variety of pollutants which have an increasing impact on urban air quality, principally carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and particulates. In addition, photochemical reactions resulting from the action of sunlight on NO_2 from vehicles, leads to the formation of ozone, a secondary long-range pollutant, impacting in rural areas, often far from the original emission site. Acid rain is another long-range pollutant influenced by vehicle NO_x emissions.

With these constraints in mind, much research is nowadays devoted to the development of devices able to discriminate NO_2 among other bi-products of polluting emissions. In particular, Phthalocyanines (Pc), their metalloderivates (MPc) and related compounds, have shown the architectural flexibility and environmental stability suitable for technological applications [1–3]. Thus, the interest of phthalocyanines, in addition to basic research, has been recently expanding also into applied fields such as photovoltaic, electrochromism, optical data storage, liquid crystals and chemical sensors, among others [4–6]. Indeed, it is well known that substances which show semiconducting or conducting properties or high linear and nonlinear optical responses are currently of great scientific and technological interest for designing electronic or optoelectronic devices [7].

In particular, phthalocyanine electrical properties change upon exposure to gases like NO_2, and the interest in developing gas detectors, having Pc derivates as the chemically sensitive component of chemical/conductometric transduction systems, is steadily increasing [8–11].

In Nitrogen dioxide two species, monomeric NO_2 (dioxide) and dimeric N_2O_4 (tetroxide), co-exist in a strongly temperature

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dependent equilibrium. At temperatures between −9.3 and 135 °C nitrogen dioxide and tetroxide coexist as a mixture of gases. In the evaluation of exposures to the mixture of these two compounds, however, the results are customarily expressed in terms of nitrogen dioxide (NO_x).

However, the interaction of nitrogen dioxide gas with phthalocyanine crystals and films results in an important effect on conductivity (6–8 orders of magnitude) and was therefore more intensively studied than the other gas interactions [12]. Most studies focused on crystalline precursor phthalocyanine powders and the many interesting results provided a useful insight into the gas-active material interaction mechanism. It is worth noticing that the conduction mechanism is due to the formation of a charge-transfer complex between the phthalocyanine donor material and the NO_2 acceptor, so that charge carriers are the holes produced in the phthalocyanine matrix [13,14].

However, the physical-chemical interaction, occurring between the material, when processed as thin film, and NO_x must be further investigated, in order to address the technological hints limiting the improvement of such sensing devices [15,16].

In particular, the scientific goal of this work is to unfold the interaction mechanism between the gas molecules and an efficient gas sensing MePc thin film, the bi[phthalocyaninato(2-)]titanium(IV) whose structure is reported in Fig. 1 [17].

An unexpected adsorption induced surface phase transition behavior when exposed to NO_x was detected [18,19]. Furthermore, the approach to this study has been highly unconventional allowing an in-situ real time monitoring of the morphological changes occurring during the gas sensing process. This was possible, both in the direct and in the reciprocal space, by means of the joint Energy Dispersive X-ray Reflectometry/Atomic Force Microscopy (EDXR/AFM) technique developed in laboratory [20].

Indeed, gas sensors are traditionally studied by optical/conductometric techniques, since the interaction with gas usually results in a change in the absorbance spectra or in conductivity. However, with this traditional approach, neither the gas-sensing physical process nor the kinetics ruling such mechanism can be observed in real time. MPcs are processed as thin films in order to act as active element of a gas sensing electro-resistive device and it has been demonstrated that their structural/morphological arrangement plays a major role in their sensing properties (recovery rates, reversibility, etc.) [21–23].

It is established that Pcs crystallize as a variety of polymorphs, ranging from amorphous to highly crystalline, existing in two predominant phases, the α form and the β form. Such structural properties can, in most cases, be modulated/obtained varying the deposition techniques/conditions and temperatures [24]. Indeed the monoclinic α-phase is traditionally more suitable for toxic gas sensors fabrication, showing a DC conductivity much higher than the triclinic β-phase. The former is typically obtained by vacuum sublimation at room temperature [25], while the latter arises when post deposition annealing are performed. On the contrary, smooth amorphous films, allowing better contacts in device fabrication, might be preferred for some applications [26,27].

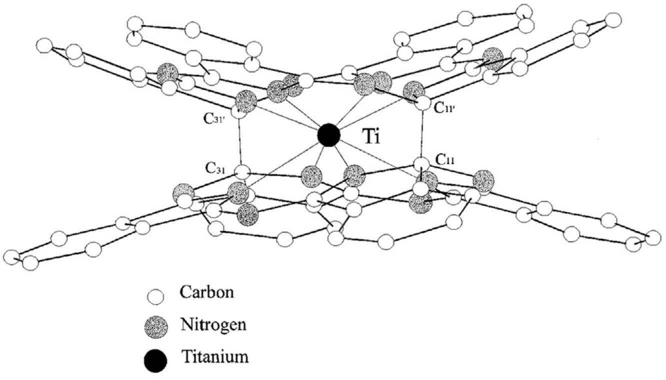

Fig. 1. The structure of a $TiPc_2$ unit is shown. The central Ti atom coordinates two phthalocyanine units connected to each other via C–C single bonds.

The study of titanium Pc thin films was approached with this constraints in mind, knowing that the material has proven good sensing performance and with the interest of unrevealing the gas adsorption mechanism. In situ time resolved EDXR is a technique able to study morphological characteristics of layered samples, being the main tool to deepen the knowledge of the basic interactions occurring inside the films matrix when exposed to NO_2 gas [28,29]. However, the roughness values obtained by EDXR represent a combined surface/interface information and, most importantly, these are mean values obtained integrating over the acquisition time. The simultaneous use of an AF microscopy, operating during the spectroscopic acquisition/gas exposure, allowed to achieve the surface related information on the adsorption mechanism, via a highly accurate time dependent surface monitoring. Indeed, the AFM topographical reconstruction can be considered as a time-resolved surface imaging process, each line of an image corresponding to a “picture” of the gas/film interaction during the AFM line acquisition (20sec.).

2. Experimental

A critical operation in the construction of a sensor is the physical deposition of the phthalocyanine film onto the electronic substrate. Generally, the morphology of the phthalocyanine films is variable and strongly affected by the sublimation conditions: it ranges from amorphous [30] to highly crystalline [31]. Furthermore, the particular conditions applied during deposition may have a pronounced effect on the final film morphologies and consequently on the response vapors. If a series of sensing films (with reproducible electronic characteristics and vapor response) are to be produced, the growth conditions, influencing morphology, uniformity and thickness must be controlled [16,21].

Vacuum sublimation is usually used for depositing most unsubstituted phthalocyanine compounds and is performed heating a small quantity of purified material at temperatures ranging from 300° to 500 °C.

All films examined in this paper were obtained by PVD vacuum sublimation according to a standard procedure [32]. Briefly, an Edwards Auto 306 vacuum coater with diffusion pumping system was used to prepare the $TiPc_2$ films on Si (100) substrates kept at R.T., and the growth was observed by an Edwards FTM5 film thickness monitor, measuring the change in the resonance frequency of a quartz crystal balance [33].

EDXR measurements were performed on a non commercial spectrometer [34]. This method was chosen since the advantages of the ED technique over the angular dispersive counterpart, mainly related to the immobility of the experimental setup, are quite remarkable regarding reflectometry measurements on evolving systems [35–37]. Indeed, the immobility of the experimental setup reduces systematic errors induced by the angular scan (misalignments and aberrations) and guarantees the reproducibility of the experimental conditions particularly critical at small angles, when many consecutive measurements have to be performed, as in the present case. This allows *in situ-time resolved* investigations to be performed with an extremely high degree of confidence [38,39].

In the present ED study, the Bremmsstrahlung of a 2 KW tungsten anode X-ray tube (supplied at 55 KV and 20 mA) was used