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Gas Sensitivity Study of Films Based on Polymeric Phthalocyanines

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Abstract:

Organic semiconductive materials are known to considerably modify their electrophysical properties on adsorption of the active gases at low temperatures. The conductivity, resistance-temperature relationship, sensor properties relative to nitric oxide, oxygen and hydrogen sulfide of films based on oligo- and polyphthalocyanines containing Co, Cu, Fe and Mn were investigated in the present work. Polymeric films were deposited on the test structures with a pair of interdigital metal electrodes formed at their surface. The investigations were carried out under the sensor thermal stabilization conditions in the range 50 - 250 ^{0}C with the constant values of the heater resistance.

Key words: polyphthalocyanine, film, gas detection

Introduction

The modern gas sensors are mainly used for ecological and technological monitoring in both stationary and, to a large extent, portable equipment. For portable devices it is important low consumption. In this case the sensor should be as sensitive as possible with the lowest operating temperature. A conductivity (resistance) of such sensors changes with a concentration of an active gas by the value, large enough to be measured by usual methods. The measurements should be reversible and stable in time.

Organic semiconductive materials are known to considerably modify their electrophysical properties on adsorption of the active gases at low temperatures. These changes are generally take place due to the formation of the complexes with the charge transfer at the donor-acceptor interaction of the sensitive layer with the determined compound. It is confirmed by high adsorptive and electrophysical activity of phthalocyanines and their analogs, which contain azaporphines macrocycles with the developed system of conjugated double bonds [1-3]. Introducing metal into the macrocycle's "window" of phthalocyanine is accompanied by the change of the electron density at the peripheral nitrogen atoms and, consequently, the change of the properties of substance.

Gas sensitivity and stability of films based on oligo- and polyphthalocyanines (OPcs and PPcs, respectively) containing Co, Cu, Fe and Mn were investigated in the present work.

Experimental

The substances were synthesized by polycyclotetramerization of tetranitrile of pyromellitic acid in bulk and in polar solvents at 180-300 ^{o}C for 5-30 hours in the presence of 0-5 mol. % carbamide. The metal content in the obtained polymers was from 0.5 to 15 wt % according to X-ray fluorescence analysis.

Polymeric films were deposited on the test structures with a pair of interdigital metal electrodes formed at their surface. The sensor's active area was 4.0x4.0 mm, and electrode gap was egual 0.08 mm. The sensitive layers were formed by two methods. The soluble OPcs were deposited from dimethylformamide solutions and insoluble PPcs were deposited by the thermal sputtering in vacuum. The films thermal sputtering was obtained at evaporation temperature of 300-1000 ^{0}C and pressure in chamber 1.33×10^{-8} bar.

The films' properties were examined on sample gas mixtures using a dynamic blender "Environics-4000" (Environics, USA) and Dräger test ampoules (Dräger, Germany). The investigations were carried out under the sensor thermal stabilization conditions in the range 50 - 250 ^{0}C with the constant values of the heater resistance and applied power.

Results and Discussion

The conductivity of the films, their resistance-temperature relationship, sensor properties relative to nitric oxide, oxygen and hydrogen sulfide as well as effect of the conditions of film formation on their characteristics was study.

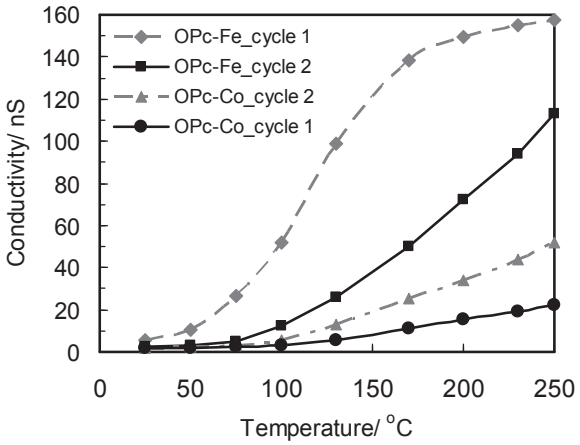

Fig. 1. Typical conductivity dependence on temperature for OPc-Co and OPc-Fe films at two serial cycles.

It was shown that preliminary temperature treatment significantly affects adsorption activity of polymeric film. The sensitive layers' characteristics changed with temperature of film in different ways that connected with composition and structure of polymeric phthalocyanine (see Fig. 1).

Films showed different sensitivity to presence of NO micro concentrations in range of 0-500 ppb in air. Resistance of polymeric film with Cu decreases up to 3 times in investigated range (see Fig. 2).

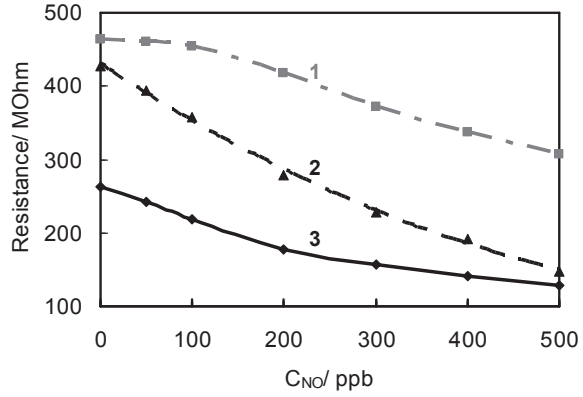

Fig. 2. Typical resistance dependence on NO concentration in air at 100 ^{0}C: PPc-Co (1); PPc-Cu (2); OPc-Fe (3).

The content of oxygen in measured medium has different influence on electro physical behavior of films. In case of OPc-Cu the resistance falls up to 2 times, and at that time for PPc-Cu films this change is smaller (see Fig. 3).

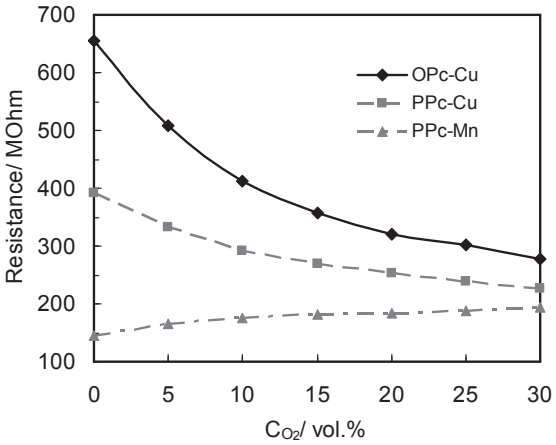

Fig. 3. Typical resistance dependence on oxygen concentration for films at 200 ^{0}C.

The conductivity of PPc-Cu decreases up to 10 times at 100-150 ^{0}C in air medium with H_2S of 0,1 ppm, while time constant does not exceed 60 s.

Despite the structure of the elementary polyphthalocyanine element is similar to the phthalocyanine structure, it exhibits a more developed conjugation system that amplifies nucleophilic properties of polyphthalocyanines. At this metal can be in different positions of the polymer that results in different electronic structures of polyphthalocyanines and must affect their adsorption behaviour, which has important role for sensitive layer's working in sensor. The metal type and content in polymeric phthalocyanine affects the electophysical characteristics and behavior at interaction with gas molecules.

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