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Passive chemiresistor sensor based on iron (II) phthalocyanine thin films for monitoring of nitrogen dioxide

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ABSTRACT

Nitrogen dioxide (NO_2) is a highly toxic oxidizing gas generally produced as a byproduct of combustion processes and also commonly stored in high concentrations as dinitrogen tetroxide (N_2O_4) for military and industrial use. A passive, unpowered sensor for the detection of NO_2 gas was achieved using iron phthalocyanine (FePc), an organometallic molecular crystal. FePc acts as an electron donor in the presence of nitrogen dioxide gas, forming a charge carrier complex that effectively dopes the FePc. The resulting decrease in resistivity was monitored to determine ambient NO_2 concentrations. FePc thin film sensors were manufactured via physical vapor deposition of FePc powder onto gold inter-digitated electrodes patterned on oxidized silicon substrates. Gas exposure tests were conducted in a Teflon PTFE test cell, with sensor resistance monitored in real time. Up to four orders of magnitude change in resistance was observed upon saturation to 100 parts per million (ppm) NO_2 equilibrated in Nitrogen (N_2) gas; sensors were tested over an extreme diurnal temperature range of −46 to 71 °C, demonstrating two orders of magnitude change at 71 ° C and up to four orders of magnitude change at −46 °C. Thermal cycling results across this temperature range indicated that sensor base resistance is mostly a function of temperature. Using normalized sensor resistance output plotted vs. time, NO_2 concentrations in the range of 0.5–2 ppm was consistently detectable. A passive FePc based NO_2 sensor can provide passive long-term monitoring of toxic NO_2 levels with high cost-effectiveness and minimal maintenance under a large operating temperature range.

1. Introduction

The danger to human health associated with exposure to nitrogen dioxide (NO_2) gas is well documented, and is known to cause symptoms ranging from permanent deterioration of pulmonary function to fatal pulmonary failure [1]. Due to increasing findings of results correlating NO_2 levels to lung disease, many governments and health agencies around the world have increasingly adopted stricter guidelines regarding safe levels of NO_2 exposure. The National Institute for Occupational Safety and Health (NIOSH), the American Conference of Industrial Hygienists (ACGIH), and the Occupational Safety and Health Administration (OSHA) have each posted recommended exposure levels to exceed no greater than 1 part per million (ppm) in volume. Aside from natural and anthropogenic sources releasing NO_2 in the atmosphere, a significant risk occurs in the space and rocket industry, where the storage and handling of large volumes of dinitrogen tetroxide (N_2O_4) is common place. N_2O_4 belongs to the family of mixed oxides of nitrogen (MON), existing in equilibrium with and readily dissociating into NO_2 when leaks occur. Used as the hypergolic oxidizer component in high performance hydrazine-based rocket propellants, N_2O_4 use is expected to extend into future NASA shuttle projects, commercial space projects, as well as various military missile projects. The result is an increased need for sensors to detect and monitor NO_2, particularly in statically contained work and storage environments.

1.1. Sensing mechanism

The family of metal-substituted phthalocyanines (MPc) has been found to be highly reactive with strong oxidizing gases such as NO_2[2,3]. Iron phthalocyanine (FePc) belongs to this family of organic molecular solids. Its composition consists of hydrogen, carbon, nitrogen, and substituted iron (II) arranged into a macrocycle. Under vacuum and without the presence of oxidizing gas dopants, FePc thin films have been found to possess band gap energies greater than 3 eV. In this state it can be considered non-conducting. However, the presence of strong electron accepting gases such as NO_2 effectively dopes FePc thin films, increasing its conductivity by many orders of magnitude. The conductivity of FePc can be described via an electron donor–acceptor mechanism, where free electrons in the FePc molecule participate in pi-bonding with NO_2 gas molecules, forming hole charge carriers that are highly mobile

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[2–5]. FePc thin films can thus be utilized in an extrinsic p-type semiconductor sensor, acting as the active sensing element that responds to NO_2 gas.

1.2. Merits of a passive sensor

Though MPcs have been found to be highly sensitive NO_2 sensors, most research have generally focused on thermally controlled MPc sensors which operate based on substrate heating and cooling to achieve sensing and cleansing cycles [6,7]. Heating the MPc film provides the thermodynamic conditions necessary for improved sensor reversibility and recovery, and at sufficient temperatures, near real time concentration determination may be achieved due to improved gas adsorption–desorption kinetics. Such active systems have been designed for monitoring NO_2 concentrations in environments where a continuous power source and a monitoring system are available [8–11]. However, active heating of MPc films tends to cause deterioration of film stability and reduce sensor longevity as film structure is altered during operation [12,13]. For the purpose of detecting NO_2 leaks in industrial or military settings within storage containers or closed environments, such as in satellites, rockets or missile silos, and industrial settings, a new passive sensor approach can be advantageous. Such applications typically employ an external container filled with inert nitrogen gas designed to contain leaks. For cost-effectiveness and long life, passive FePc sensors may be placed within the external container and monitored without the need for a constant power source, to serve as a simple unsafe NO_2 level indicator. A suitable passive sensor should also remain stable and responsive within a large temperature range, due to the lack of substrate heating. In this research, a passive, chemical resistance based, thin film FePc sensor was designed and fabricated in attempt to provide simple and long-term monitoring of hazardous levels of NO_2 gas in a nitrogen controlled environment for temperatures between − 46 and 71 °C.

2. Sensor design and fabrication

2.1. Substrate design

The NO_2 gas sensor consists of an active layer of FePc thin film deposited upon a gold inter-digitated electrode pattern. The interaction between FePc and NO_2 gas is that of a surface adsorption induced charge–carrier transfer complex [3,6], thus NO_2 gas molecules adsorbed onto FePc films effectively dopes the film, altering its electrical conductivity. The change in electrical properties of FePc thin films is monitored via resistance measurements across the underlying electrodes. The design for the inter-digitated electrode pattern is shown in Fig. 1.

The spacing between electrode fingers is a constant 15 μm. An ohmic type contact is expected at the FePc–electrode interface. At this spacing, the applied voltage required for detection is within 1 V, allowing the use of simple resistance monitoring circuitry or handheld multi-meter devices. A UV mask containing 360 individual sensor patterns for use with 4 in. round wafers was created and used to make sensors used in this research. An advantage of inter-digitated electrode designs is such that the specific region within the active layer experiencing the largest conductivity increase becomes the path of least resistance. This represents a favorable condition overall, because it allows the part of the deposited film that possesses the best conductivity characteristics to control the output signal.

2.2. Fabrication

Fabrication of the sensor was based on common microelectronics fabrication procedures. Standard practices for wafer cleaning, oxidation, photolithography, and material deposition were performed in the setting of a clean room. The main steps in the fabrication process are diagrammed in Fig. 2.

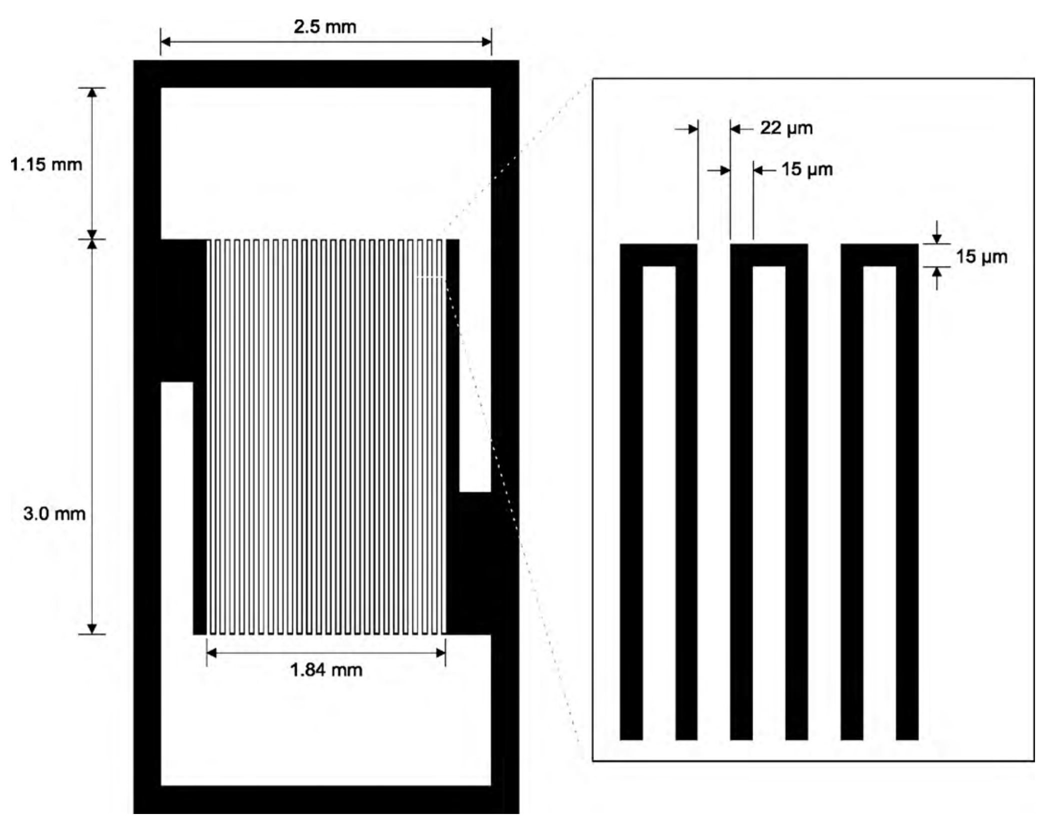

Fig. 1. Sensor inter-digitated electrode pattern consists of two main electrode contacts for interface with measurement circuitry. The two main electrodes branch into 25 pairs of parallel electrode fingers. FePc thin film is deposited above the electrodes to serve as the active layer.