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Preparation and characterisation of $ZnFe_2O_4/ZnO$ polymer nanocomposite sensors for the detection of alcohol vapours

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Abstract

During the last 10 years, a large interest has developed in the preparation of nanocomposite structures by embedding inorganic nanoparticles into polymeric materials. These materials combine the properties of the inorganic fillers with the processability and flexibility of polymers. The versatility of polymer nanocomposite systems is of special interest to the gas sensor industry where arrays of polymer/carbon black composites have been used to identify gases and odours. These polymer gas sensors provide selectivity based on their chemical structures and operate at room temperature, which provide advantages over thick-film metal oxide gas sensors. $ZnFe_2O_4$ and ZnO have excellent stability, high sensitivity, low fabrication complexity and moderate operating temperatures, which are ideal properties for a gas sensing material. In this work, the development of a thick-film $ZnFe_2O_4/ZnO$ sensor, which operates at room temperature and a drop-coated conducting polymer composite sensor containing 30 w/w% $ZnFe_2O_4/ZnO$ nanoparticles is discussed. The sensors were tested in a fully automated test rig and showed promising results for the detection of alcohol vapours.

Keywords: Nanocomposite materials; Polymer; Metal oxide; Gas sensor; Thick film; Room temperature

1. Introduction

In recent years, interest has grown in the use of low powered gas and vapour sensing devices for applications such as homeland security, integrated system health management,

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non-destructive evaluation and remote sensing [1]. Large industrial plants that produce and store large quantities of highly toxic and flammable liquids like propanol require highly sensitive and selective vapour sensing systems [2]. These systems are used to monitor the background environment of the workers and prevent exposure to vapour levels over the maximum allowed exposure limits.

Further developments in handheld detection systems have brought about the use of e-nose devices for fast, non-invasive medical diagnostics based on the identification of trace levels of organic compounds in the breath [3]. The use of these systems could become widespread and improve on existing diagnostic procedures currently in place. Volatile organic compounds (VOCs) are present in exhaled air at concentration levels that correspond to their blood concentrations multiplied by their ambient vapour pressure. The human breath contains approximately 200 compounds, some of which have been connected to various diseases. These compounds can be identified using a laboratory-based analysis of the exhaled air. However, it is a complex, expensive and time consuming process. As a result, its use is not widespread. The introduction of sensor devices capable of real-time detection could allow the analysis of human breath at clinics and hospitals quickly, as a cost effective, non-invasive procedure [3].

The sensitivity, selectivity and stability of metal oxide materials make them ideal candidates for gas sensing applications. These materials generally operate at high temperatures but recent developments have shown that the combination of these materials with a polymer binder allow room temperature operation [4,5]. The sensitivity and selectivity of the sensors can be manipulated based on the choice of binder where the Flory–Huggins interaction parameter as shown in Eq. (1) can be used as a means to determine the most suitable polymer binder for the vapour or gas to be detected.

$$\chi_{12} = \frac{V_S}{RT}(\delta_S - \delta_P)^2. \tag{1}$$

From Eq. (1), V_S is the molar volume of the solvent (cm^3/mol^{-1}), T is the temperature (K), $R = 8.314$ J mol^{-1}, δ_S is the solubility parameter of the vapour ($J^{1/2}$ $cm^{-3/2}$) and δ_P is the solubility parameter of the polymer ($J^{1/2}$ $cm^{-3/2}$). The closer the value $(\delta_S - \delta_P)^2$ is to zero the higher the level of interaction between the polymer and vapour resulting in greater sensitivity.

The aim of this paper is to compare the sensitivity of thick-film and drop-coated $ZnFe_2O_4/ZnO$/polymer composite sensors to that of propanol vapour at increasing concentrations. These devices, which work at room temperature, are believed to be a cost-effective alternative to commercially available gas sensors.

2. Experimental

2.1. Electrode preparation

An E306A Edwards coating system was used to evaporate thin films of Cu onto alumina substrates. A layer of photoresist was spin coated onto the Cu and allowed to dry for 24 h. Electrode patterns were designed using Eagle PCB software and printed on acetate. The pattern was UV exposed onto the substrate, developed and etched as described in [6].

2.2. Thick-film paste preparation and sensor fabrication

60:40 mol.% Fe_2O_4/ZnO powders were wet-ball milled in alcohol for 24 h and dried at 120 °C. This powder was then pressed into a pellet under 2 tons of pressure and fired at 1250 °C