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Formaldehyde gas sensor based on silver-and-yttrium-co doped-lithium iron phosphate thin film optical waveguide

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ABSTRACT

Several formaldehyde gas sensors were fabricated using silver-and-yttrium-co doped-lithium iron phosphate ($LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$)-thin-film-based optical waveguides (OWGs). $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ powders with different concentrations of the dopants Ag and Y were prepared in high purity via a one-step hydrothermal method, and characterized using their X-ray diffraction patterns and energy dispersion spectra. The obtained powders were subsequently utilized in a spin-coating procedure for the fabrication of $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ thin films.

The obtained thin films were characterized by refractive index, thickness, attenuation, and sensing properties to formaldehyde at room temperature. The response of $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$-thin-film/tin-diffused-glass-based optical waveguide sensors to formaldehyde was higher than their responses to other VOCs. For a set of formaldehyde concentrations ranging from 1 ppb to 1000 ppm, the sensitivity of the sensors increased with a decrease in the dopant concentrations. Moreover, the ability to be used repeatability as well as the selectivity of the sensors was tested using lower gas concentrations; at the lower concentrations (below 250 ppm), the sensor only responsive to formaldehyde gas.

1. Introduction

The evaluation of indoor air quality is a serious environmental issue that needs to be addressed urgently. Formaldehyde (CHOH) is one of the harmful volatile organic compounds (VOCs) emitted by building materials, interior decoration materials, wood furniture, carpets, and so on. Formaldehyde gas irritates human eyes and noses at concentrations higher than 200 ppb, causes breathing difficulties above concentrations of 5 ppm, and has been known to be a carcinogen since 1980 [1,2]. The World Health Organization (WHO) has established a concentration of 0.08 ppm, averaged over 30 min, as a standard for long-term exposure to formaldehyde vapors [3], while the Chinese Environmental Protection Agency (EPA) established 0.06 ppm as the standard [4].

Several sensors have been reported for formaldehyde detection. These include enzyme-based biosensors [5], metal-oxides-based gas sensors [6], piezoelectric sensors [7], and optical fiber sensors [8]. Among the various kinds of sensors, optical chemical sensors have been shown to be safe for use in an explosive environment, in addition to be applicable in unusual or extreme conditions [9]. The optical waveguide (OWG) sensor [10,11] is of particular interest owing to its high sensitivity, fast response time, low cost, and intrinsically safe detection.

A simple planar OWG consists of a substrate, a thin top layer (waveguide layer) with a refractive index greater than that of the substrate (onto this, a sensitive covering material is deposited to detect the analyte), and the covering material (usually air). In this study, $LiFePO_4$ co doped with Ag and Y ($LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$) was used as the sensing element for a formaldehyde gas sensor. $LiFePO_4$, which has an olivine structure, has attracted great interest as the cathode material in rechargeable lithium-ion batteries because of its high energy density, low cost, low toxicity, excellent thermal stability, and safety [12–14]. So far, a number of experimental studies on $LiFePO_4$ have appeared that have improved its electrochemical properties through doping with other elements [15,16], prepared $LiFePO_4$ thin film electrodes [17], and used it lithium-ion sensors [18]. However, there is almost no report on its optical properties as well as the gas sensing applications.

After enormous experiment confirm that, $LiFePO_4$ thin film exhibited excellent optical transparency [19–21], easy fabricated, high refractive index, good response to pollutant gases, and was a qualitative candidate for optical waveguide gas sensor.

In semiconductor gas sensor, the gas-sensitivity has been improved by introducing dopants or decreasing particle size of sensing materials [22]. Previously [20,21], the sensitivity and

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selectivity of $LiFePO_4$ thin film OWG were improved by doping Ag and Y, separately. In this study, in order to get more sensitive material, both Ag and Y were selected as dopants.

Herein, we report the development of a $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$-thin-film/tin-diffused glass-based OWG sensor and its application in formaldehyde gas detection. Our research focused on the effect that the concentrations of the dopants, Ag and Y, used to fabricate the $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ thin film, had on the gas sensing properties of the sensor with respect to formaldehyde gas.

2. Experimental methods

2.1. Preparation of $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ powders

$LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ powders were synthesized by a hydrothermal method. Iron (II) sulfate heptahydrate (analytically pure), phosphoric acid (85 wt%; analytically pure) and lithium hydroxide monohydrate (analytically pure) were mixed in a molar ratio of 1:1:3 [23]. In order to simplify the synthesis process, $AgNO_3$, Y $(NO_3)_3{\cdot}6H_2O$ and 0.1 g of ascorbic acid were added to form $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ (x = 0.5, 1.0, 2.0). The resulting solution was placed in a hydrothermal reactor having an inner volume of 100 cm^3, and the hydrothermal process was performed at 150 °C for a period of 15 h. The mixture was allowed to cool down to room temperature, was filtered, and the product was collected and dried under vacuum at 120 °C for 1 h. X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (DPMax 2400, Japan) using graphite-mono chromatized Cu Kα radiation(λ = 1.5418 Å). Elemental analyses of the $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ powders were performed using Oxford 2000 energy disperse spectroscope (EDS). In addition, the crystal sizes of the products were also calculated (Table 1).

2.2. Fabrication of the sensing films and the measurement of their attenuation, thickness, refractive index

The sensing films were prepared as follows: (1) the $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ powder (0.02 g) was dissolved in 10 $cm^3$of a solvent [a mixture of phosphate acid (1.4 wt%), ascorbic acid (3 wt%), and polyvinyl alcohol (1.5 wt%)]. (2) The obtained $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$ solution was coated onto the surface of a tin-diffused glass OWG (n = 1.52 with the guiding layer being 1–2-μm deep) using a spin-coater over a period of 25 s at a rotation speed of 1700 rpm. (3) After the spin-coating process, the coated film was placed in a vacuum desiccator for 24 h at room temperature. In order to determine the solvents (H_3PO_4-Vc-PVA) efficacy in formaldehyde detection, the H_3PO_4-Vc-PVA thin film based OWG (not added the silver-and-yttrium-co doped-lithium iron phosphate) was prepared using the same process, and was used to test VOCs.

With the aim of investigating the porosity of the sensing film, a set of samples were heat treated in air at 450 °C for 30 min. As reported in a previous study [19], at this treating temperature, the refractive index of the $LiFePO_4$ film is high. The porosity of the sensing film was obtained from Yoldas' expression, which is given below [24]:

$$P = 1 - \frac{n^2 - 1}{n_d^2 - 1}$$

where P is the pore volume fraction, n the refractive index of the porous film, and n_d the refractive index of the film after complete densification.

The thickness and refractive index of the sensing film were determined using a Tianjin SGC-10 ellipsometer. The attenuation in the thin film due to absorption and scattering was measured using the cut back method [25]. The output light intensity (I_1) of the thin-film OWG (the length of the thin film was L_1) was measured using an apparatus for testing optical waveguides (Fig. 1). After that, the length of the film was shorten to L_2 and the output light intensity (I_2) was measured again. The attenuations (dB/mm) were calculated using the formula give below (Table 2):

$$\text{Attenuations (dB/mm)} = 10 \log \frac{I_1/I_2}{L_1 - L_2}$$

2.3. Procedure for testing for gas

The gas testing apparatus, shown in Fig. 1, was contained compressed air sources and comprised a $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$-thin-film-based OWG gas-sensitive element, laser sources, a flow meter, a reflector, a diffusion tube, a light detector (photomultiplier), and a recorder (computer). The $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$-thin-film-based OWG gas-sensitive element was fixed to the testing apparatus, and a semiconductor-based laser beam (650 nm) was introduced into the $LiFe_{1-0.01x}Y_{0.005x}Ag_{0.005x}PO_4$-thin-film-based OWG using a prism coupler and it emerged from another prism coupler. The distance between the two prism couplers was 15 mm. The intensity of the output light was monitored using a photomultiplier detector, and the signal was recorded by a computer. For each measurement, a new syringe was used to inject 20 cm^3 of the gas sample into the flow chamber that then flowed out from the vent (Fig. 1). Pure air, which functioned both as a carrier and dilution gas, flowed through the cell at a constant rate of 50 cm^3 min^{-1} in order to transfer the sample gas to the sensor. The flow cell (with dimensions of 2 cm × 1 cm × 1 cm) was mounted on a rotating stage equipped with XYZ translation. All measurements were performed at room temperature.

Standard formaldehyde gas was obtained by vaporizing a given amount of a formaldehyde solution (99.5%) inside a standard vessel (600 cm^3). The concentration of the formaldehyde gas was confirmed using a commercial formaldehyde gas detection tube (Gastec). Different amounts of the standard formaldehyde gas were diluted with pure air in a second standard vessel (600 cm^3) in order to obtain the desired concentrations. Using this standard-vessel-dilution method, very low concentrations of formaldehyde (in the ppb range) could be obtained.

Table 1
Crystal size of sensing materials.

Sample	$LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$	$LiFe_{0.99}Y_{0.005}Ag_{0.005}PO_4$	$LiFe_{0.98}Y_{0.01}Ag_{0.01}PO_4$
β_{011} (rad)	0.00314	0.00269	0.00361
β_{111} (rad)	0.00272	0.00269	0.00248
β_{121} (rad)	0.00361	0.00360	0.00271
β_{131} (rad)	0.00361	0.00252	0.00234
D_{hkl} (nm)	43.8	50.1	52.3