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Optical and electrochemical gas sensing properties of yttrium–silver co-doped lithium iron phosphate thin films

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ABSTRACT

The new sensing material, $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ was synthesized using hydro-thermal methods, and characterized by X-ray diffraction, energy dispersive spectroscopy and X-ray photoelectron spectroscopy. The as prepared products were subsequently utilized in a self assembled optical waveguide gases testing apparatus and a WS-30A electro-chemical gas sensing apparatus for xylene detection. A glass optical waveguide gas sensor was fabricated by spin-coating a $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ thin film on the surface of single-mode tin-diffused glass Optical Waveguide. The sensing elements for electro-chemical gas sensor were made by dip-coating a $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ thin film on the surface of an alumina ceramic tube, assembled with platinum wire. The experimental results indicated that, at room temperature, $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ thin film/tin-diffused optical waveguide sensing element exhibited higher response to xylene in the range of 0.1–100 ppm; at an optimum operating temperature (300 °C), the response (S_r) of $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ to 100 ppm of xylene was 5.29, as measured by the WS-30A electro-chemical gases sensing apparatus.

1. Introduction

The demands for accurate and dedicated sensors to monitor and control environmental pollution have accelerated the development of sensor technology and new sensing materials over the last few decades [1]. Amongst the various techniques developed to fabricate chemical sensors, the Optical Waveguide (OWG) [2,3] methods are of particular interest owing to their attributes for being small in size, high sensitivity, fast response time, ability to be monitored at room temperature and intrinsically safe detection. Furthermore, they suffer little or no interference in the waveguide element of the sensor and can be manufactured at a very low cost.

Numerous materials were reported to be usable as chemical sensor [4–6], and some new types of sensing materials are still being studied and exploited currently. Lithium iron phosphate ($LiFePO_4$) is used as an active cathode element for new generation lithium-ion batteries because of its low cost, no toxicity, and remarkable thermal stability [7]. However, $LiFePO_4$ has one main drawback and that is its low electrical conductivity [8].

Thus, many reports about the experimental study of $LiFePO_4$ to improve its electrochemical properties through particle optimizing, metal doping [9,10], and mixing with electrically conductive materials like carbon, metals, and metal oxides [11] have appeared. The increase of electrical conductivity was deduced to the increase of refractive index of sensing materials [12]. While, in OWG gas sensor, the increase of refractive index was dedicated to improvement of gas sensitivity of sensing materials [13–15]. In order to improve the gas sensitivity of $LiFePO_4$, both Ag and Y were selected as dopants. To the best of our knowledge, there is no report on $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ thin film gas sensor. In this study, silver–yttrium co-doped $LiFePO_4$ was synthesized using hydro-thermal methods by one step, through X-ray diffraction, energy dispersive spectroscopy, and X-ray photoelectron spectroscopy testing, the doping contents

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and valence state of Fe in $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ materials were studied. The optical-electrical gas sensing properties was monitored by a self assembled optical waveguide (OWG) gases testing apparatus and a WS-30A electro-chemical gases sensing apparatus.

2. Experimental

2.1. Synthesis of $LiFe_{0.995}Y_{0.0025}$ $Ag_{0.0025}$ PO_4

The sensing material ($LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ powder) was synthesized using the hydro-thermal method [16]. $FeSO_4 \cdot 7H_2O$, 85 wt% H_3PO_4, and $LiOH \cdot H_2O$, all analytically pure, were mixed in the molar ratio 1:1:3. Then, $Y(NO_3)_3 \cdot 06H_2O$, $AgNO_3$ ($Y+Ag:LiFePO_4=0.5:99.5$) and 0.1 g of ascorbic acid were added, respectively. The resulting mixture was placed in a hydrothermal reactor (inner volume: 100 ml), and hydrothermal synthesis was carried out at 150 °C for 15 h. After allowing it to cool naturally and filtering, the prepared sample was 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-monochromatized Cu Kα radiation ($\lambda=1.5418$ Å). Elemental analyses of the $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ powders were performed using Oxford 2000 energy dispersive spectroscopy (EDS).

2.2. Fabrication of the thin film OWG sensing element

The sensing film was prepared as follows: (1) The $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ 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 $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ 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 treated at 450 °C for 30 min. As reported in a previous study [12], at this treating temperature, the $LiFePO_4$ film refractive index exhibited high values. X-ray photo-electron spectroscopy (XPS, AXIS Ultra) was used to detect the oxidation state of Fe in $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ thin film. The sensing film thickness and refractive index were determined using a Tian Jin SGC-10 ellipsometer.

2.3. Benzene/Toluene/Xylenes (BTX) testing

The Benzene/Toluene/Xylenes (BTX) gases testing apparatus (Fig. 1) was contained in compressed air sources, a flow meter, reflector, laser sources, gas mixing manifold that contained BTX gases, $LiFe_{0.995}Y_{0.0025}Ag_{0.0025}PO_4$ film/Tin-diffused glass OWG gas sensing element, photomultiplier detector and recorder (PC). A gas mixing manifold was used to mix the air stream that contained BTX gases with a stream of pure air and to introduce the mixture into the flow cell, which enclosed the waveguide sensor. The flow cell (2 cm × 1 cm × 1 cm) was mounted on a rotational stage equipped with X–Y–Z translation. The semiconductor laser beam (650 nm) was introduced into the OWG using a prism coupler (glass prism, $n=1.78$; and a matching liquid, di-iodomethane, $n=1.74$), and it emerged from another

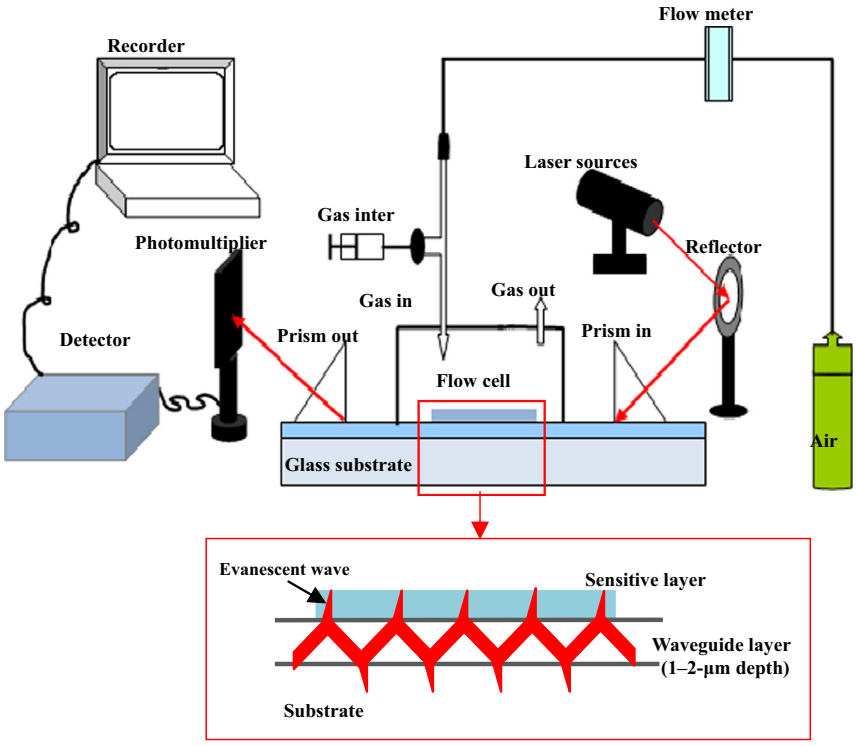

Fig. 1. Schematic view of optical waveguide (OWG) sensor system.