Applied Surface Science 257 (2011) 10763–10770

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis of nanorods and mixed shaped copper ferrite and their applications as liquefied petroleum gas sensor

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ARTICLE INFO

Article history:
Received 2 March 2011
Received in revised form 21 July 2011
Accepted 22 July 2011
Available online 28 July 2011

Keywords:
LPG sensor
$CuFe_2O_4$
Surface morphology
Poly-ethylene glycol (PEG)

ABSTRACT

Present paper reports the preparation and characterization of nanorods and mixed shaped (nanospheres/nanocubes) copper ferrite for liquefied petroleum gas (LPG) sensing at room temperature. The structural, surface morphological, optical, electrical as well as LPG sensing properties of the copper ferrite were investigated. Single phase spinel structure of the $CuFe_2O_4$ was confirmed by XRD data. The minimum crystallite size of copper ferrite was found 25 nm. The stoichiometry was confirmed by elemental analysis and it revealed the presence of oxygen, iron and copper elements with 21.91, 12.39 and 65.70 atomic weight percentages in copper ferrite nanorods. The band gap of copper ferrite was 3.09 and 2.81 eV, respectively for nanospheres/nanocubes and nanorods. The sensing films were made by using screen printing technology and investigated with the exposure of LPG. Our results show that the mixed shaped $CuFe_2O_4$ had an improved sensing performance over that of the $CuFe_2O_4$ nanorods, of which a possible sensing mechanism related to a surface reaction process was discussed. Sensor based on mixed shaped copper ferrite is 92% reproducible after one month. The role of PEG in the synthesis for obtaining nanospheres/nanocubes has also been demonstrated.

1. Introduction

Liquefied petroleum gas (LPG) is a flammable gas which presents many hazards to both the humans and environment. LPG is being used as fuel for domestic and industrial purposes. Increasing usage of LPG has increased the frequency of accidental explosions due to leakage, because combustion accidents might be caused when it leaks out accidentally or by mistake. Thus the requirements for reliable and sensitive gas detecting instruments have increased for safety at home as well as industries. Therefore, LPG sensor has become the subject of intense research today in view of fundamental research as well as industrial applications. In spite of considerable efforts, good sensors for LPG have not been found till now, the problem being of crucial importance for industrial as well as domestic purposes. LPG sensing at room temperature is of great interest as various LPG sensors reported basically work at higher temperature such as 250 °C, but it is not convenient for commercial point of view. To realize this goal, much attention has been focused on the study of LPG sensors [1–3]. Semiconductor gas sensors in the form of thin or thick films, based on metal oxides such as SnO_2, ZnO, TiO_2 and p–n hetrojunctions, have been widely reported in the literature [4–7]. Current years have been seen the increased interest in searching new semiconducting materials for gas sensor application. Some well known materials for LPG sensing are ZnO [8], modified-ZnO (viz., CoO–ZnO, zinc–gallate, zinc–titanate, cobalt–zincate), SnO_2, WO_3 and doped materials etc. [9–11].

Spinels of the type $M^{2+}M_2{}^{3+}O_4$ attract the research interest because of their versatile practical applications [12–15]. In the case of M^{3+} (M = Fe), the resulting spinel ferrites having a general chemical composition of MFe_2O_4 (M = Cu, Mn, Mg, Co, Zn, Ni, Cd, etc.) are widely used as magnetic materials [16–18]. Reddy et al. studied the ferrites prepared by wet chemical precipitation as gas sensing materials [19]. They reported the response of zinc ferrite for H_2S and that of nickel ferrite for Cl_2. Tianshu et al. reported the response of cadmium ferrite for ethanol sensor [20]. Currently it is a topic of increasing interest to study the gas sensing properties of ferrites [21–29].

The LPG sensing mechanism of such type of sensors involves the chemisorptions of oxygen on the surface of sensing material, followed by charge transfer during the reaction of oxygen with LPG molecules, which will cause a resistance change on the surface of sensing elements [30]. The adsorption of gas on the surface of a semiconductor is responsible for significant change in the electrical resistance of the materials; there have been a sustained and

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doi:10.1016/j.apsusc.2011.07.094

successful effort to make use of this change for purpose of gas detection.

In our previous papers, we have reported spherical- and nanonails-shaped ferric oxide nanoparticles and studied its LPG sensing properties [31,32]. Here mixed shaped (nanocubes/nanospheres) and nanorods of copper ferrite were prepared by co-precipitation method using cupric and ferric chlorides with and without PEG, respectively. The influence of the surface morphology on the LPG sensing properties of copper ferrite was investigated. The role of PEG polymer in the synthesis for obtaining uniform sphericals/nanocubes like surface morphology was also demonstrated.

The objective of our research is to determine the best sensing material for the LPG detection. Here we have synthesized copper ferrite with different surface morphologies and its LPG sensing properties were investigated. The sensitivity of these sensing elements to LPG is found better than our previously reported work [31–34].

2. Experimental details

2.1. Synthesis of $CuFe_2O_4$

A chemical co-precipitation method was used for the synthesis of nanocrystalline $CuFe_2O_4$. The stoichiometric amount of starting materials, such as cupric chloride ($CuCl_2{\cdot}2H_2O$) and ferric chloride ($FeCl_3{\cdot}6H_2O$) were taken and dissolved in required amount of ethanol. In addition to this, some drops of poly-ethylene glycol was added for synthesis of copper ferrite nanocubes/nanospheres, while nanorods were prepared without PEG. Both solutions (cupric and ferric chlorides) were magnetically stirred at 80 °C for 1 h to get homogeneous solution. Then both were mixed to each other with initial atomic weight ratio of copper and iron precursor was 4:1. In addition to this, ammonium hydroxide solution was added drop by drop to the above mixed solution and a black colored precipitate was obtained. This co-precipitation reaction was carried out at 80 °C with pH of solution 12. Further this was mechanically stirred at room temperature for 6 h and obtained precipitate was filtered and washed several times with deionized distilled water until the pH of the filtrate became 7. Took it as paste and prepared thick films on alumina substrate using screen printing thick film technology. These films were allowed to stabilize at room temperature for 6 h and then these were annealed at 500 °C for 2 h and silver contacts on both sides of the films were made for signal registration. This thermal treatment is an important process for the stabilization of the semiconducting material which converted the films as sensing elements. The annealing of the sensing element at high temperature has been reported by many authors to achieve long term stability, higher sensor response and short response time [35,36]. During thermal treatment the oxygen species are adsorbed in the forms of O_2^-, O^- and O^{2-} on ferrite surface, which are highly reactive towards incoming gas molecules. Therefore, these oxygen species play an important role in the gas sensing phenomenon. The thickness of the film was found 4 μm measured by accurion variable angle spectroscopic ellipsometer (Nanofilm EP3 Imaging).

2.2. Characterization techniques

The synthesized powder was characterized for their structural investigations by X-ray diffractometer (X-Pert PRO PANalytical). The XRD data of synthesized material was recorded by using Cu K_α radiation having wavelength $\lambda = 1.5406$ Å. The intensity was collected over 2θ range 20–70°. The crystallite size of the samples was calculated by Debye–Scherrer's equation. The surface morphologies of the sensing films were observed by scanning electron microscope. Energy-dispersive X-ray spectroscopy (Zeiss; Supra-40), was used for identifying the elemental composition of the sensing materials at 20 KV accelerating voltage. Optical characterization was done by using UV–visible absorption spectrophotometer (Varian, Carry-50 Bio) in UV and visible region.

2.3. Measurements of gas sensing characteristics

For the LPG sensing measurements, the sensing film with silver contacts was placed with in a specially designed gas chamber having gas inlet and an outlet. Now this was exposed with the LPG and the variations in electrical resistance of the sensing material with the time were recorded by using a Keithley electrometer. Gas sensing properties of films were measured for different vol.% of LPG at room temperature. The sensitivity of sensing element is defined as the slope of the resistance–time curve and is given below [33]:

$$S = \frac{\Delta R}{\Delta t}$$

The sensitivity of the sensor is to be high due to a large change in resistance (ΔR) in a short time (Δt) in the presence of LPG, and for an enhanced performance it is desired that both the changes occur accordingly. If more and successive change is found in electrical resistance of the sensing element under investigation, the more will be the sensitivity of the sensor.

Percentage sensor response for the sensing material is defined as [33]:

$$\%\text{S.R.} = \frac{\left|R_a - R_g\right|}{R_a} \times 100$$

where R_a and R_g are the resistance values of the sensor in air and gas–air mixture, respectively.

2.4. Electrical measurements in air (resistance–temperature characteristic)

For measuring the electrical properties of sensing elements in air, the sensing elements were put inside a tubular furnace at the highest point of temperature profile with electrical connections and variations in electrical resistance with temperature were recorded. The used heating rate was 2 °C per minute. The temperature dependent resistance measurement shows the thermally activated exponential behaviour of copper ferrite.

3. Results and discussion

3.1. Scanning electron microscopy analysis

Fig. 1(a) and (b) shows SEM images of copper ferrite with PEG, at different magnifications. These images show mixed shaped (nanocubes/cuboids/nanospheres) surface morphology. It is clearly seen from the micrographs that the particles of the $CuFe_2O_4$ are at nanoscale. This is very advantageous for gas sensing applications as smaller particles have a large specific surface area and as a result an elevated response to LPG. Fig. 2(a) and (b) shows SEM images of copper ferrite without PEG, at two different magnifications. These images reveal the uniform and compact distribution of rods type surface morphology. The average length and diameters of rods are ~400 and 120 nm. While Fig. 1(a) and (b) exhibits mixed shaped surface morphology and few particles appear to be close to a spherical shape with particle size ~40 nm, some particles are found to be agglomerated, but these images show better porosity as a number of active sites for gas adsorption are present. These results obviously entail that PEG influences the shape of the resulting product.