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Investigation on effects of surface morphologies on response of LPG sensor based on nanostructured copper ferrite system

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ABSTRACT

Synthesis of a copper ferrite system ($CuFe_2O_4$) via chemical co-precipitation method is characterized by X-ray diffraction, surface morphology (scanning electron microscope) and optical absorption spectroscopy. These characteristics show their dependence on the relative compositions of the two subsystems. They are further confirmed by the variation in the band gap.

A study of gas sensing properties shows the spinel $CuFe_2O_4$ synthesized in 1:1 molar ratio exhibit best response to LPG adsorption/resistance measurement. Thus resistance based LPG sensor is found robust, cheap and may be applied for kitchens and industrial applications.

1. Introduction

Liquefied petroleum gas (LPG) is an inflammable gas, which presents many hazards to humans as well as environment. The leakage of LPG is a serious problem as its lower explosive limit (LEL) is 1.8 vol.% [1]. This makes the LPG sensors very interesting for both in basic research and industrial applications. LPG sensors are helpful in environmental monitoring, home safety and chemical controlling as well. Nanostructured materials can enhance the performance of LPG sensor because of their much higher surface-to-volume ratio as compared to coarse micro grained materials [2–6]. In addition to the enhanced sensitivity demonstrated by use of the nanostructured materials, the sensors can give a quick response too. However, it should be noted that the effects of grain size are often complicated by other factors for instance heat treatment of the sensor during manufacturing. Grain size and porous structure have a major effect on the gas-sensing properties of polycrystalline materials and their full characterization should be the first step in the study of materials [7–9].

Searching of new materials in order to develop high performance solid-state gas sensors is one of the main stuff. Various semiconducting oxides in the forms of bulk, thick and thin films have been investigated as gas sensing materials [10–12]. Ferric oxide (α-Fe_2O_3) is one of the most technologically important semiconductors since it is traditionally used as pigments, anticorrosive agents, magnetic materials, sensors as well as burn-rate catalyst in composite propellants. This is due to its low cost, high resistance to corrosion, temperature dependent surface morphologies and environment friendly properties [13–16]. Spinel-type oxides are an alternative for inexpensive and robust detection systems because of good chemical and thermal stability under operating conditions [17–19]. There has been much interest in spinel-structural compounds (general formula AB_2O_4) because of their unique catalytic action and gas-sensing properties [20–25]. Therefore, fine metal particles of ferrites are receiving increased attention due to their applications in preparation of high density ferrite cores, as suspension materials in ferromagnetic liquids, as catalysts, adsorbents and sensors. The ultra fine particles of ferrites are found to alter the electrical, magnetic, electro-optical and chemical properties through a wet chemical synthesis of successive hydrolysis, oxidation and dehydration of ferrous chloride, and decomposition of metal carboxylates [26]. Therefore it is a topic of increasing interest to study the gas sensing properties of ferrites [27–31].

The sensing mechanism of the gas sensor is based on the change in the electrical resistance of sensing pellets resulting from the chemical reactions between LPG and adsorbed oxygen at the ferrite surface [32–34]. The interaction between the gas molecules and the surface of the sensing pellet depends on its surface morphological structure [9]. The surface morphology has an

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important role on the sensitivity of solid-state gas sensors [35,36]. The nano grained materials provide new opportunities for enhancing the performance of gas sensors because of their high surface to volume ratios.

In the present investigation the LPG sensing properties of various pellets of nanostructured copper ferrite system synthesized via chemical co-precipitation method have been reported. The synthesis of copper ferrite was carried out without using any exothermic reaction in order to achieve the ultrafine well-dispersed highly dense particles. The objective of the present work is to study the development of structural, optical and surface morphologies of copper ferrites in order to understand the effect of these on the response of the sensor. These studies show that copper ferrite system synthesized in various molar ratio exhibits significant variation in LPG sensing properties. Thus we found that the surface modification of the ferric oxide pellet by copper ferrite is an effective method for enhancing the sensor response of ferric oxide based LPG sensors. The appearance of CuO on the surface of ferric oxide improves the rate of adsorption of gas molecules. This paper also reports the effect of surface morphologies on the LPG sensing characteristics by carrying out the co-precipitation reaction employing different molar ratios of $CuCl_2$:$FeCl_3$.

The sensitivity of the LPG sensor fabricated here is found better in comparison to our previously reported work [36–39]. Therefore, present work deals with the advancement in the modification of surface morphologies as well as LPG sensing characteristics.

2. Experimental details

2.1. Synthesis of $CuFe_2O_4$

A chemical co-precipitation method was used for the synthesis of nanocrystalline powder of $CuFe_2O_4$. The stoichiometric amounts of starting materials such as cupric chloride ($CuCl_2{\cdot}2H_2O$) and ferric chloride ($FeCl_3{\cdot}6H_2O$) were taken in a 1:1, 1:2, 1:3 and 1:4 molar ratios and dissolved in required amount of isopropyl alcohol to form 1 M solution. The solution was magnetically stirred at 80 °C for 1 h to get homogeneous solution. After that ammonium hydroxide solution was added drop by drop to the above solution and a black colored precipitate was obtained. This co-precipitation reaction was carried out at 80 °C and pH 12. Later the solution was mechanically stirred at room temperature for 6 h. Further the precipitate was filtered and washed several times with distilled water until the pH of the filtrate became 7. The resulting material was dried at 100 °C for 3 h and then annealed at 500 °C for 2 h to obtain the fine powder of copper ferrite. The whole procedure was repeated for synthesis of $CuFe_2O_4$ in 1:2, 1:3 as well as 1:4 molar ratios. The crystalline powder annealed at 500 °C was crushed into fine powder using a pestle and mortar. This powder was used to prepare gas sensing materials in the form of pellet using hydraulic press (MB instruments, Delhi) under an uniaxial pressure of 616 MPa. Hereafter, the copper ferrite pellets in 1:4, 1:3, 1:2 and 1:1 molar ratios were named as P-1, P-2, P-3 and P-4 sensing pellets respectively. Each pellet was 9 mm in diameter and 3 mm in thickness.

2.2. Characterization techniques

The synthesized powder of copper ferrite in different molar ratios was characterized for structural investigation by X-ray diffractometer (X-Pert PRO PANalytical). The XRD data was recorded using CuK_α radiation having wavelength λ = 1.5406 Å. The intensity was observed over 2θ range 20–70°. The crystallite sizes of the samples were calculated by Debye–Scherrer's equation. The surface morphologies of the sensing pellets were analyzed using scanning electron microscope (SEM, LEO Cambridge). Energy-dispersive X-ray (EDAX) spectroscopy (Zeiss; Supra-40) was used for identifying the elemental compositions of the sensing materials at 10 kV accelerating voltage. Optical characterization was done using UV–vis absorption spectrophotometer (Varian, Carry-50 Bio) in UV and visible ranges.

2.3. Measurements of gas sensing characteristics

For the gas sensing measurements, the sensing pellet was inserted within a specially designed gas chamber having gas inlet and outlet knobs [37]. Before passing of the LPG in the chamber, the gas chamber was stabilized in air for 10–15 min. The stabilized resistance of the pellet was taken as stabilized resistance in presence of air (R_a). Now the pellet was exposed to LPG and the corresponding variations in electrical resistance of the sensing material with the time due to the chemical surface interactions were recorded using a Keithley electrometer (Model: 6514A). Gas sensing properties of the sensing materials were measured for different vol.% of LPG at room temperature. The sensitivity/response speed of the sensing pellet is defined as the slope of the resistance–time curve and is given as below [38,39]:

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

Percentage sensor response for the sensing material is defined as [40]:

$$\%SR = \frac{|R_a - R_g|}{R_a} \times 100$$

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

3. Results and discussions

3.1. Surface morphological investigations

Fig. 1(a) and (b) shows the surface morphologies of copper ferrite synthesized in 1:4 molar ratio at magnification 60 and 150k× respectively. These micrographs show the rods like structure and some particles appear as random spheres. Fig. 2(a) and (b) shows the surface morphologies of copper ferrite synthesized in 1:3 molar ratio at magnification 60 and 150k× respectively. Fig. 3(a) and (b) exhibits the surface morphologies of copper ferrite synthesized in 1:2 molar ratio at nanoscale and microscale respectively and surface morphologies of copper ferrite synthesized in 1:1 molar ratio at magnification 175 and 250k× are shown by Fig. 4(a) and (b) respectively. It is evident from the SEM images described above that the grains of the copper ferrite are at nanoscale with vivid pores. This is much more advantageous for gas sensing applications as smaller grains have a larger specific surface area and as a result an elevated response to LPG. The grain size distribution was uniform in all the cases. Among them Fig. 4(a) and (b) shows spherical surface morphology and large number of active sites are there. The particle sizes of these nanospheres are ~60 nm and the surface has a number of pores. These pores serve as gas adsorption sites wherein the reaction of LPG with adsorbed oxygen takes place. Thus LPG diffuses through these pores and subsequent reactions occur.

It is well known that the gas-sensing properties of metal oxides are strongly depending on their surface morphological features. A high reactive surface area with oxygen vacancies facilitates the chemisorptions process by increasing the adsorption and desorption rates. The grain neck and grain boundary feature also influences the gas sensing properties. The smaller grain size increases gas sensitivity since the diameter is comparable with or