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Growth of zinc ferrite aligned nanorods for liquefied petroleum gas sensing

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ABSTRACT

Present paper reports the fabrication of zinc ferrite thin film sensor having two different types of surface morphologies (mixed shaped nanorods and vertically aligned nanorods) and their growth mechanism. The LPG sensing properties of the vertically aligned assembled nanorods are found improved significantly in comparison to mixed shaped nanorods. When we compare our sensor performance with other thin film sensors, it is found that the sensor performance obtained in this work is definitely better than that of others. Thus our investigation demonstrates the potential application of aligned nanorods in the fabrication of LPG sensor operable at room temperature.

1. Introduction

For the sensing applications, the microstructure such as grain and pore sizes, dimensionality of the nanostructures, surface to volume ratio and film thickness plays a critical role [1,2]. In traditional pellet or thick film based gas sensors, due to higher thickness, the gas molecules cannot enter up to the bottom of the film. So due to the reduction of the utility factor, response to the analytes (target gas) also reduces to a great extent [3,4]. As these sensors operate on the principle of both surface and bulk conductivity changes, hence the performance of these sensors is also reduced [5]. However, due to the small thickness, the response of thin film based gas sensors are primarily based on the surface conductivity changes [6]. Additionally, if the thin film sensing material is porous, the gas molecules can easily enter and react with the whole volume of the material, thus increasing the response of the sensor. As a result, controlled growth of nanostructures is of great importance in the field of sensors [7]. In view of above argument, here in our synthesis we have paying attention for the controlled growth of aligned zinc ferrite porous nanorods.

Recently, gas sensors based on 1-D nanostructures have been fabricated with enhanced gas-sensing properties [8–11]. These gas sensors are based on either single nanowire or entangled nanowires film without any alignment [8–10]. However, vertically aligned nanorods may enhance the response than entangled nanorods due to more exposed surface area. Vertically aligned nanorods arrays provide a simple matrix to study the average effect of the assembled nanorods. Therefore, in the present investigation the results concerning the morphological evolution and sensing properties of aligned nanorods are focused.

2. Experimental

$ZnFe_2O_4$ was synthesized via sol–gel method using stoichiometric amounts of the starting materials such as $ZnSO_4 \cdot 7H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ taken in 1:2 molar ratios respectively. These materials were dissolved separately in appropriate amount of ethanol to from 0.1 M solution. The obtained precursors were magnetically stirred at 80 °C for 2 h. Further, both precursors were mixed with each other and the resulting precursor was magnetically stirred for 6 h, ensuing in the formation of zinc ferrite gel. Now, the prepared gel was divided in to two parts. In the first part 20 ml of polyethylene glycol (PEG) was added drop by drop under continuous stirring. PEG works as a capping agent and controlled the agglomeration of the particles. This gel was used for the fabrication of thin film on alumina substrate (10×10 mm^2) using spin coater (Metrex Scientific Instruments, India) at 2000 rpm for 60 s. The fabricated film was dried at 120 °C for 6 h. This drying process stabilized the film. Further it was annealed at 500 °C for 3 h at a heating and cooling rate of 5 °C/min. This process converts the film as sensing material and we labeled this film as G-1.

Another part of the gel was used for the fabrication of next thin film and we labeled this film as G-2. It is worth mentioning that we will investigate the role of PEG on the surface morphology as well as LPG sensing properties. The thickness of films G-1 and G-2

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were ~300 nm measured by accurion variable angle spectroscopic ellipsometer (Nanofilm EP3 Imaging). Further, the sensing films (G-1 and G-2) were analyzed with scanning electron microscope (SEM, LEO) to identify the surface morphology. Particle size distribution has been investigated by acoustic particle sizer (APS-400, Matec). For the study of the sensing properties, silver electrodes were grown on two opposite ends of the film. Further it was inserted in to the sensing chamber for measurements of temporal resistance for different concentrations of the gas. The details of the sensing chamber are given in our previous publication [3].

3. Results and discussion

Fig. 1(a) shows the surface morphology of film G-1 i.e., zinc ferrite with PEG. It is clear that the nanocrystalline and porous zinc ferrite mixed shaped rods are formed. The length and diameter of the rods are ~250 and 35 nm respectively, with narrow size distribution controlled by PEG. The linear chains of PEG can be cross linked in aqueous medium [12] i.e., in ethanol. The cross-linking between the chains may provide small cages wherein the reactant mixture gets trapped. Further, during annealing, the reactant mixture trapped in the cages converted in to nanorods of zinc ferrite. Thus, the cages formed by cross-linking may offer resistance to the agglomeration of the particles and exhibited separate nanorods. Fig. 1(b) illustrates the surface morphology of film G-2. It shows interconnected-aligned nanorods, form an open porous network which assurance a good interaction between the nanorods surface and the surrounding gas atmosphere. Each nanorod in Fig. 1(b) has diameter in the range of 25–45 nm and is interconnected to other one. This kind of surface morphology may give the better surface area for the gas to interact. The size estimations by SEM are in good agreement with the particle diameter calculated using the acoustic particle sizer (Fig. 1(c)).

One interesting aspect in Fig. 1(b) is that the number of surface atoms becomes a significant fraction of the total number of atoms for the aligned nanorods, therefore such category of aligned 1-D surface morphology and its surface energy plays a significant role in enhancing the sensitivity of the sensor. Such types of aligned nanorods are stable due to its lowest Gibbs free energy for this growth. The assembled nanorods minimized their total surface energy. This surface energy may be reduced through (i) surface relaxation i.e., the surface atoms shift inwardly, (ii) surface restructuring through combining surface dangling bonds into strained new chemical bonds, (iii) surface adsorption through chemical or physical adsorption of chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or vander Waals forces, and (iv) composition segregation or impurity enrichment on the surface through solid-state diffusion. As shown in Fig. 1(b), maximum rods are aligned and this would definitely help better transduction during gas sensing measurements. Fig. 1(d) presents the elemental analysis of aligned nanorods and reveals the presence of Zn, Fe, O and S.

The aim of the present paper is to study the LPG sensing performance of G-1 and G-2 film sensors. Variations in electrical resistance with time for different concentrations of LPG were recorded for G-1 and G-2, shown in Fig. 2(a) and (b) respectively. Each curves of Fig. 2(a) and (b) show that as time increases the resistance of the film decreases drastically in the beginning and afterwards it decreases slowly and becomes saturated. Further, when the outlet of the chamber was opened, the resistance of the film increases sharply and then slowly until it attains the value of stabilized resistance in air (R_a). As shown in Fig. 2(b), the resistance of G-2 sensor drops more rapidly, when LPG is introduced into the testing atmosphere, indicating a good response capability of this sensor. The variations of percentage sensor response for G-1 and G-2 as a function of concentrations of LPG are shown by Fig. 2(c). Sensor G-2 shows rapid response to LPG than G-1 and the maximum responses were 206 and 435 %

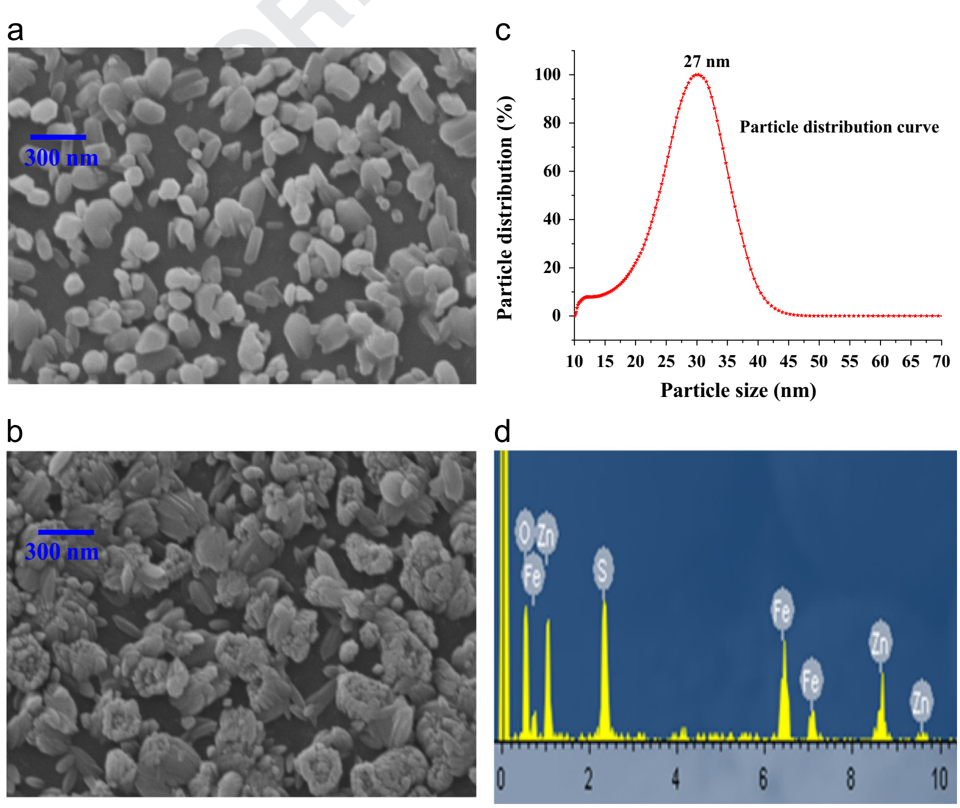

Fig. 1. SEM image of: (a) G-1 and (b) G-2, (c) particle size distribution curve, (d) EDAX of G-2.

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