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Copper doped nickel ferrite nano-crystalline thin films: A potential gas sensor towards reducing gases

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HIGHLIGHTS

- $Cu:NiFe_2O_4$ thin films are synthesized by low cost spray pyrolysis technique.
- Addition of Cu content improves magnetic properties.
- Cu content on the surface of the film enhances the gas response.
- $NiFe_2O_4$ thin films exhibit predominant selectivity towards ethanol.
- 1 wt% $Cu:NiFe_2O_4$ film responses towards ethanol at lower optimum temperature.

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ABSTRACT

$NiFe_2O_4$ and (1 wt% and 3 wt%) $Cu:NiFe_2O_4$ thin films have been fabricated using spray pyrolysis deposition technique at 350 °C and then sintered at 650 °C for 3 h. X-ray diffraction, SEM, EDAX, UV-VIS spectroscopy, SQUID VSM were carried out to investigate phase formation, microstructural and influence of Cu doping on magnetic properties of $NiFe_2O_4$ thin films. The gas response towards various gases viz. ethanol, Liquid Petroleum Gas (LPG), methanol and hydrogen sulfide (H_2S) is investigated. The results of XRD revealed that all samples had shown the principal phase of nickel ferrite and the lattice parameter was found to vary from 8.294 Å to 8.314 Å on an incorporation of Cu, and the crystalline sizes were about 40–45 nm. The effect of Cu concentration on saturation magnetization and coercive force were studied. The maximum value of saturation magnetization calculated from hysteresis loop was 89.16 emu/g at room temperature and 96.88 emu/g at 50 K. Cu content on the film surface was found to be maximum for 1 wt% $Cu:NiFe_2O_4$ thin film and this film showed an improved response towards all gases. Response of ethanol for $NiFe_2O_4$ thin film was found to be higher as compared to all the other gases. The lowering of the optimum operating temperature is observed in 1 wt% $Cu:NiFe_2O_4$ thin film with higher selectivity towards ethanol than other gases. All results indicated that the Cu doping in nickel ferrite thin films has a significant influence on the properties.

1. Introduction

Semiconductor gas sensors have been expansively investigated for many different applications such as environmental monitoring, automotive applications and air conditioning in airplanes, spacecrafts and house. Moreover, recently semiconducting nanostructures have earned attention due to their huge surface to volume ratios. A gas sensors performance is strongly dependent on the sensor materials surface area. In 1991, Yamazoe demonstrated that reduction in crystal size would significantly increase the sensor performance [1]. This is because nano-sized grains of metal oxides are almost depleted of carriers (most carriers are trapped in surface states) and exhibit much poorer conductivity than micro-sized grains in ambient air, hence, when exposed to target gases, they exhibit greater conductance changes as more carriers are activated from their trapped states to the conduction band than with micro-sized grains.

In general, metal oxides are conventionally used to detect most of the reducing gases but their limited selectivity, reproducibility and thermal stability are common problems related to the composition and microstructure of the relevant materials. Semiconductor gas sensors are usually derived from ceramic processing

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and thick film technology. However, they are difficult to miniaturize and are incompatible with integrated circuit fabrication technology. Some of these problems can be overcome using nanometer thin films prepared via physical and chemical routes. Moreover noble metal additives with high effective oxidation catalytic activity can be used to enhance the sensitivity of such sensors. Kapase et al. [2] synthesized Ni–Zn ferrites by citrate sol-gel method and addition of Pd in Ni–Zn ferrite shows improvement in sensitivity and response time towards ethanol. Kadu et al. [3] found that the addition of Pd improves the sensitivity, response and reduces the operating temperature from 300 °C to 230 °C of Mn–Zn ferrite towards ethanol. Influence of Pd on LPG sensing properties of magnesium ferrite was studied by Darshane et al. [4] and observed highest response and lowering in operating temperature from 350 °C to 200 °C.

In this context, from last few years, researchers have focused on thin films for gas sensors [5–7]. Thin films have good selectivity, enhancement in surface area, low operating temperatures and fast response, though only moderate sensitivity because of various reasons such as crystallite size, high defect density, texture, grain boundaries, substrate used and fabrication methods.

Nickel ferrite ($NiFe_2O_4$) has been widely studied as a magnetic material [8,9] and considered as gas sensor in the bulk form towards chlorine [10], hydrogen sulfide [11], acetone [12] and LPG [13]. However, the gas sensing properties nickel ferrite in thin film form towards the reducing gases is not explored much. Microstructural, magnetic, electric and dielectric properties of Cu containing nickel ferrite have been investigated earlier [14,15]; though, there are no reports on Cu doped nickel ferrite thin films as a gas sensor. Hence it is appealing to study the gas sensing properties of Cu doped nickel ferrite for reducing gases.

Various methods have been used for deposition of ferrite thin films viz. RF sputtering [16], plasma laser deposition (PLD) [17] etc. These methods usually involve elaborate and costly apparatus and complicated process. Furthermore, the high deposition temperature limits the option of the material of the substrates and thus limits the application of the ferrite thin films. Spray pyrolysis technique is versatile and has the unique advantage of producing large surface-area films (about 2″ × 2″) at low cost. It involves a simple experimental setup and lowers the processing temperatures required to arrive at a stable phase. The response of material as a gas sensor primarily depends upon its pore size, porosity and specific surface area. From our earlier studies [18] it is experienced that these parameters can be controlled easily using spray pyrolysis deposition technique by varying deposition parameters. At the same time doping can be done without many efforts for desired percentage using this technique.

In the present work, Cu:$NiFe_2O_4$ thin films were deposited on Si (100) and alumina and their structural, magnetic, optical and gas response properties towards ethanol, LPG, methanol, H_2S were studied.

2. Experimental

2.1. Synthesis of $NiFe_2O_4$ and Cu:$NiFe_2O_4$ thin films

$NiFe_2O_4$ and Cu:$NiFe_2O_4$ ($NiFe_2O_4$ + 1 wt% and 3 wt% Cu) thin films were deposited using dual mode automated spray pyrolysis system on Si (100) (5 mm × 2 mm) and alumina (5 mm × 5 mm) substrates which were cleaned prior to the deposition. Si wafer was dipped for 30s in 1:20 HF:DI water to remove the native oxide layer and any contamination in the oxide from the wafer surface and then strongly rinsed in DI water. The alumina substrates were cleaned using soap solution and distilled water. Then subjected to ultra-sonicator bath and lastly dried under IR lamp. An aqueous ethanol solution of nickel chloride [$NiCl_2.6H_2O$] and iron (III) chloride [$FeCl_3$] (mole ratio 1: 2) were chosen as the precursor solutions for the deposition of $NiFe_2O_4$ thin film. The molar concentration of the precursor solution was kept 0.15 M. For the deposition of Cu:$NiFe_2O_4$ thin films an aqueous solution of copper chloride [$CuCl_2.2H_2O$] (1 and 3 wt%) was added in the precursor solution. All chemicals used were of AR Grade (99.99%). Compressed air was employed as the carrier gas. The solution was sprayed by a spray gun and the resulting mist was deposited on to the Si (100) and alumina by compressed air at a flow rate of 15–17 lpm. The substrate temperature was maintained at 350 °C during the deposition. The deposition time depends on the volume of the spraying solution. The nozzle-substrate distance was kept fixed at 30 cm. During decomposition reaction, metal reacts with oxygen, and finally resulted in brown coloured uniform ferrite thin film. After deposition, the coated substrates were allowed to naturally cool down to room temperature before being taken out from the spray chamber. The deposited thin films were then air annealed at 650 °C for 3 h to obtain single phase spinel structure.

The structural characterization of these nickel ferrite thin films deposited on Si (100) was carried out using Bruker AXS D8 diffractometer, with CuK_α radiation. The surface morphology of all the samples was studied using JEOL, JSM 6360A scanning electron microscope (SEM). Reflectance measurements of all the films deposited on Si (100) were carried out using Perkin–Elmer spectrophotometer in 200–1100 nm range. The thickness of ferrite films was measured using Talystep Profilometer and they were found to be about 6 μm for all the films. M–H curves of ferrite thin films deposited on Si (100) and annealed were recorded using LOT-Quantum Design MPMS Superconduting Quantum Interference Device (SQUID) Vibrating Sample Magnetometer (VSM).

2.2. Gas sensitivity measurements

The gas-sensing characteristics of $NiFe_2O_4$ and Cu:$NiFe_2O_4$ thin films deposited on alumina using spray pyrolysis and air annealed at 650 °C for 3 h were studied. The sensor material was kept on a heater provided with two probes for electrical measurements in a cylindrically shaped stainless steel chamber (20 cm dia × 10 cm height). The gas response was measured after providing the ohmic contacts to the films using silver paste. The known amount of test gas was introduced in the chamber. The gas-sensing characteristics at different temperatures (T ~ 200 °C–400 °C) were recorded using a Keithley 2400 source meter.

3. Results and discussion

3.1. Structural studies

The $NiFe_2O_4$ and Cu:$NiFe_2O_4$ thin films were sintered at 650 °C for 3 h and characterized using X-ray diffraction (XRD) technique to obtain structural information. The well resolved peaks in the XRD patterns (Fig. 1) clearly indicate the polycrystalline nature of ferrite and match well with the characteristic diffraction peaks of Ni ferrites (JCPDS card # 74-2081). The observed peaks in Fig. 1 for the planes (220), (311), (222), (400), (422) and (511) confirmed the phase formation of $NiFe_2O_4$ with cubic spinel ferrite structure. Few peaks of SiO_2 are also observed in XRD patterns as SiO_2 had grown during the deposition of thin films on Si (100). However, it can be noticed that diffraction lines become broader with Cu incorporation. The crystallite size and lattice structure are known to have their own contributions to the X-ray diffraction peaks, the diffraction peaks in the XRD patterns are strong and sharp, indicating high crystallinity of all the samples.

The X-ray diffraction patterns are studied in detail for the