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Chlorine gas sensing performance of palladium doped nickel ferrite thin films

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ABSTRACT

$NiFe_2O_4$ and Pd:$NiFe_2O_4$ (Pd = 1 w/o, 3 w/o and 5 w/o) thin films, p-type semiconducting oxides with an inverse spinel structure have been used as a gas sensor to detect chlorine. These films were prepared by spray pyrolysis technique and XRD was used to confirm the structure. The surface morphology was studied using SEM. Magnetization measurements were carried out at room temperature using SQUID VSM, which shows ferrimagnetic behavior of the samples. The reduction in optimum operating temperature and enhancement in response was observed on Pd-incorporation in nickel ferrite thin films. Faster response and recovery characteristic is observed Pd-incorporated nickel ferrite thin films. The long-term stability is evaluated over a period of six months. This feature may be regarded as a significant facet towards their practical application as gas sensors.

1. Introduction

Now-a-days, it has become necessary to monitor toxic and harmful gases such as CO, NO_x, SO_x, Cl_2 and H_2S at lower level of concentration. Human exposures to toxic levels of chlorine are generally accidental as the release of high levels of chlorine is virtually always unintentional. Chlorine plays a major role in the most serious environmental problems which we face today; depletion of the ozone layer, global warming and acid rain. The pollution caused by its widespread use has been linked to a variety of serious health effects; poisonings have occurred in the chlorine industry since its inception and chlorine compounds have accumulated in the body fat of animals and humans.

Chlorine inhalation toxicity can occur during routine attendance at swimming pools, and in higher-level exposures at swimming pools when accidents occur with systems used for water purification [1,2] during military exposures, following transportation accidents, upon industrial exposure, with misuse of domestic cleaners, and, more recently, as a result of chemical terrorism.

The forms of chlorine involved in respiratory toxicity are not limited to chlorine gas, but also can include hypochlorous acid, chlorine dioxide, and chloramine. Chlorine exposure can result in injury to the eyes, skin and upper airways as well. The airway is especially affected from the nose to the level of the bronchi [3]. Repeated exposure to chlorine in the pool has been postulated to be a significant risk factor for an excess of asthma among swimmers [4].

So there is tremendous need of chlorine gas sensor which can detect the gas at very low level of concentration. Sensors based on semiconducting oxide like SnO_2, ZnO_2 and WO_3 have been widely studied as gas sensors, however selectivity remains the main challenge for such materials. Hence, there is always a search of new gas sensor material. Apart from magnetic and electronic uses now ferrites are the subject of interest for gas and humidity sensing applications [5,6].

Nickel ferrite nanoparticles are reported as gas sensor for various gases like H_2S, Cl_2, LPG whereas nickel ferrite thin films as gas sensors are not explored much. Thin film has advantage like high surface area, fast recovery, lower energy input, device compatibility, miniaturization and overall cost effectiveness. It has been shown that the gas sensing properties can be much improved by doping the ferrites with noble metals [7,8].

In the present work, we have deposited $NiFe_2O_4$ and Pd-doped $NiFe_2O_4$ thin films using spray pyrolysis technique. The effect of Pd doping in $NiFe_2O_4$ thin films for chlorine gas sensing properties is investigated.

2. Experimental

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

$NiFe_2O_4$ and Pd:$NiFe_2O_4$ (1, 3 and 5 w/o) thin films were deposited using automated spray pyrolysis system. 0.15 M aqueous ethanol solutions of $NiCl_2$ and $FeCl_3$ (mole ratio 1: 2) were used as

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the precursor for the deposition of $NiFe_2O_4$ thin films. Aqueous solution of $PdCl_2$ (1, 3 and 5 w/o) was added to this solution to obtain Pd:$NiFe_2O_4$ thin films. These films were deposited on both Si (100) and alumina substrates. Si wafer was cleaned with HF:DI (1:20) and then washed thoroughly with DI water to remove the native oxide layer and any contamination in the oxide from the wafer surface. The alumina was cleaned using soap solution, and then washed with distilled water. Both the substrates were then ultrasonically cleaned with distilled water prior to deposition. 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 nozzle-substrate distance was kept fixed at 30 cm and the substrate temperature was maintained at 350 °C and during deposition. After deposition, the coated substrates were allowed to naturally cool down to room temperature. Deposited thin films were then air annealed at 650 °C for 3 h.

The crystal structure of the nickel ferrite thin films deposited on Si (100) was investigated using Bruker AXS D8 diffractometer, with CuK_α radiation. The surface morphology of all the samples was examined using JEOL, JSM 6360 A scanning electron microscope (SEM). Thickness of the ferrite films was measured using Talystep Profilometer and they were found to be about 3 μm for all the films. The magnetic properties of ferrite thin films deposited on Si (100) were investigated using LOT-Quantum Design MPMS SQUID VSM.

2.2. Gas sensitivity measurements

The gas-sensing characteristics of $NiFe_2O_4$ and Pd:$NiFe_2O_4$ thin films deposited on alumina were studied using static setup. The gas response was measured after providing the ohmic contacts to the films using silver paste. The sensor material was kept in a steel chamber to perform sensitivity measurements towards Cl_2 gas. The gas sensing characteristics at different temperatures were recorded using a Keithley 2400 source meter. Stability of thin films and response-recovery characteristics were also studied.

3. Results and discussion

3.1. Structural studies

All the $NiFe_2O_4$ and Pd:$NiFe_2O_4$ thin films were analyzed using X–ray diffraction (XRD) technique. For XRD analysis, films deposited on Si (100) were used. The XRD patterns (Fig. 1) show

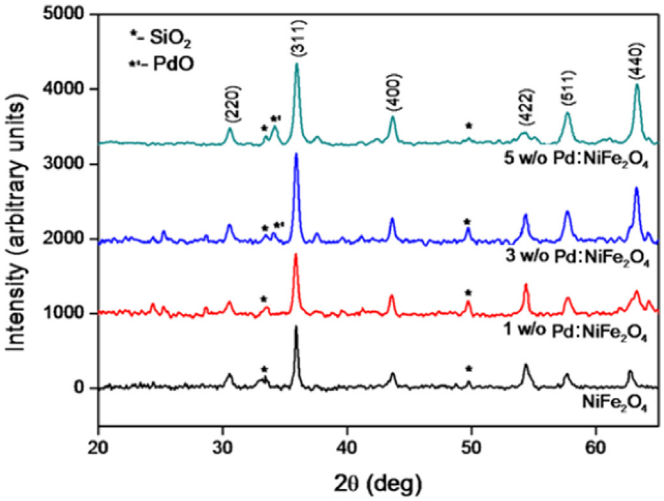

Fig. 1. XRD spectra of $NiFe_2O_4$ and Pd:$NiFe_2O_4$ thin films.

Table 1
Parameters calculated from XRD.

Sample	*Crystallite size from XRD* (nm)	*Lattice constant* (Å)
$NiFe_2O_4$ thin film	46	8.303
1 w/o Pd:$NiFe_2O_4$ thin film	38	8.288
3 w/o Pd:$NiFe_2O_4$ thin film	35	8.285
5 w/o Pd:$NiFe_2O_4$ thin film	30	8.277

single cubic spinel phase of the $NiFe_2O_4$ according to JCPDS card # 74–2081 for all the samples. The additional phase PdO is observed with 3 w/o and 5 w/o Pd doping in $NiFe_2O_4$. A small contribution of SiO_2 is observed which was formed during the deposition. Scherrer's formula, given by Eq. (1) [9] was used to calculate the average crystallite size, t, which are tabulated in Table 1.

$$t = \frac{0.9\lambda}{\beta \cos\theta_b} \tag{1}$$

where β is the angular line width at half maximum intensity and θ_b is the Bragg angle for the actual peak.

XRD shows the variation in crystallite size between 30 and 46 nm. The incorporation of Pd show remarkable decrease in crystallite size which in turn increases the surface area. It is an established fact that the grain growth depends upon the grain boundary mobility [10]. A plausible reason for the decreasing trend of crystallite size (Table 1) is that the increasing concentration of Pd reduces the grain growth probably due to segregation on or near the grain boundaries which hampers its movement. The lattice constants of these films were calculated using indexing method [11] given by Eq. (2),

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{N} = \text{constant} \tag{2}$$

where $N = n^2(h^2+k^2+l^2)$. These lattice constants are also tabulated in Table 1 which shows reduction with increase in Pd concentration.

Pd^{2+} (r=0.86 Å) ions enter into the tetrahedral lattice sites (A) of the spinel lattice. With the entering of Pd^{2+} ions some of the Fe^{3+} (r=0.67 Å) ions transform to Fe^{2+} (r=0.83 Å) ions for maintaining the charge neutrality. An increase in the population of Pd^{2+} cations and a decrease in the Fe^{3+} cations in the A site contributes to the decrease in radius of tetrahedral site while an increase in the population of Fe^{2+} cations in the A site increases the radius of tetrahedral site. Also to relax the strain some of the Fe^{2+} ions will be migrated to the octahedral site. Because of all these changes the change in the lattice constant is observed.

3.2. Morphological studies

The spray deposited films had very good adherence to the substrates. SEM images of all the thin films deposited on Si (100) are shown in Fig. 2. It is observed that $NiFe_2O_4$ thin film exhibits petal like structure whereas Pd:$NiFe_2O_4$ thin films posses agglomerates of the petals.

EDAX of Pd:$NiFe_2O_4$ thin films confirm the presence of small amount of Pd along with Ni, Fe and O are shown in Fig. 3. Various elemental ratio calculated from EDAX are tabulated in Table 2. It is confirmed that Pd/Ni ratio increases with increase in doping concentration of Pd. This increase in Pd concentration on the surface results in catalytic effect which in turn increases the sensitivity towards Cl_2 gas (discussed later in Section 3.3).