Porous spinel-type oxide semiconductors for high-performance acetone sensors

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Abstract—**Spinel-type semiconductor compounds represent an alternative for robust and inexpensive detection systems, due to their good thermal and chemical stability in operation. The sensing mechanism is based on the change in electric resistivity when exposed to specific gaseous ambient, resulting from chemical reactions between metal-oxide surface and gas molecules. Sample composition and morphology are key factors in determining the selectivity and sensitivity of solid-state sensors. In this work structural, morphological and sensory characteristics of some porous oxide semiconductors with spinel-type structure ($Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_{4-\delta}$, $Li_{0.5}Sm_{0.1}Fe_{2.4}O_4$ and $Mg_{0.9}Sn_{0.1}Fe_2O_4$) are presented. The self-combustion technique was used to prepare these compounds. This method offers the advantage of obtaining nanosized reproducible and porous ceramics with high specific surface area and exact stoichiometry. Investigated compounds hold promise for high-performance applications in acetone sensors.**

Keywords—nanoelectronics, materials for electronics, spinel-type oxide, self-combustion, acetone sensors.

I. INTRODUCTION

Years ago, it has been discovered that gas particles (atoms and/or molecules) interact with semiconductor surfaces and thus influence the surface properties of compounds, in particular its conductivity and surface potential. Seyama (1962) and Taguchi (1970) were among the first to examine gas detection using semiconductor sensors. These semiconductor sensors, as gas sensors, can be largely used both in household and industrial domain for alarms of gas leaks, process control or air pollution control. As compared to organic semiconductors (phenanthrene, polybenzimidazole) and the elementary ones (Si, Ge, GaAs, GaP), the oxide semiconductors can be successfully used as sensitive materials for detecting different gases: carbon monoxide and dioxide, hydrogen, alcohol, water vapors, ammonia, oxygen, nitrogen oxides, etc. Both *n*-type (tin, titanium and zinc oxides) and *p*-type semiconductor oxides can be used as sensor elements.

The most intensely used oxide semiconductor material is SnO_2. Increasing the conductivity of SnO_2 caused by surface reactions between the oxygen from the pre absorbent surface and reductive gases is used in detecting concentration of reducing gases. Basically, a semiconductor gas sensor functions as a resistor sensitive to gas. There were lots of tryouts done in order to modify detection characteristics of these gas sensors with oxide semiconductors in order to obtain a high sensitivity and selectivity. The improvement of sensitive properties was more or less done by developing unique preparation methods (such as thin layers, thick layers or sol-gel method) and by transition metals in the sensor material. The nanosized porous materials offer relevant opportunities for enhancing gas sensor performance, due to their high surface-area-to-volume ratio, promising absorption and desorption, respectively [1-6].

Thus, for obtaining new gas sensing materials, the preparation method used, composition and morphology play an essential role. The spinel-type oxide semiconductor compounds, of general formula AB_2O_4, have proved themselves to be suitable for detection applications of both reducing and oxidizing gases [7-13, 25-30]. Kapse V.D. [14] conducted a study on the sensitivity of spinelic oxide compounds ($NiFe_2O_4$, $ZnFe_2O_4$, $MgFe_2O_4$, $ZnAl_2O_4$, $CoAl_2O_4$ and $MgAl_2O_4$) synthesized by citrated sol-gel technique for various gases (H_2S, NH_3, C_2H_5OH, LPG).

The author obtains the best values of the magnesium spinel ($MgFe_2O_4$) sensitivity to H_2S (4.8), C_2H_5OH (12.4), LPG (6.3) at working temperature of 325 ^oC, and $CoAl_2O_4$ spinel to NH_3 (1.3) at a working temperature of 150 ^oC and 50 ppm concentration. Sutka et al [15] have studied the nickel ferrite with zinc substitutes ($Ni_{1-x}Zn_xFe_2O_4$), *p*-type semiconductors with increased porosity, predominantly open pores. The samples were synthesized by the sol-gel self-combustion procedure. In the case of $NiFe_2O_4$ sample, for a concentration of 500 ppm acetone vapors in the air, they obtain a sensitivity S of 3.7 at an optimal operating temperature of 275 ^oC.

In this work a series of oxide semiconductor compounds is presented, with spinel-type structure with high performance in the detection of acetone vapors. The compounds were obtained by self-combustion method and display *p*-type ($Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_4$) and *n*-type ($Li_{0.5}Sm_{0.1}Fe_{2.4}O_4$ $Mg_{0.9}Sn_{0.1}Fe_2O_4$) semiconductor characteristics.

II. EXPERIMENT

Three samples with chemical formulae $Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_4$ (NCM), $Li_{0.5}Sm_{0.1}Fe_{2.4}O_4$ (LS) and $Mg_{0.9}Sn_{0.1}Fe_2O_4$ (MS) were synthesized by self-combustion technique; metal nitrate and ammonium hydroxide were used as raw materials [3,8,16-18]. The synthesis technology using self-combustion technique is schematically presented in Fig. 1; more details on the procedure have been reported in Refs. 19-28. The phase composition, lattice parameters and crystallite sizes of thermally treated powders were determined by X-ray diffraction (XRD) analysis. The samples morphology was examined by Scanning Electron Microscopy (SEM).

For the gas sensing experiments, the sensor element (disk with two comb-type silver electrodes) was placed in an installation providing control of the working temperature and acetone concentration. The acetone sensing properties have been examined at various working temperatures ranging between 100 to 420 °C. The sensitivity, *S*, is defined by the relation

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a}, \qquad (1)$$

where R_a and R_g denote the sensor resistances in air and atmosphere of the test gas, respectively [15,17,18,25, 27,28].

III. RESULTS AND DISCUSSION

A. *Structural properties*

From the XRD analysis performed for the samples presented, it was found that they present a cubic structure of spinel-type as a result the heat treatments in air, specific for each sample (Table 1). Thermal treatment parameters, together with structural characteristics of actual samples, obtained from X-ray diffractometry and SEM analyses [3,8,16,18, 30] are shown in Table 1.

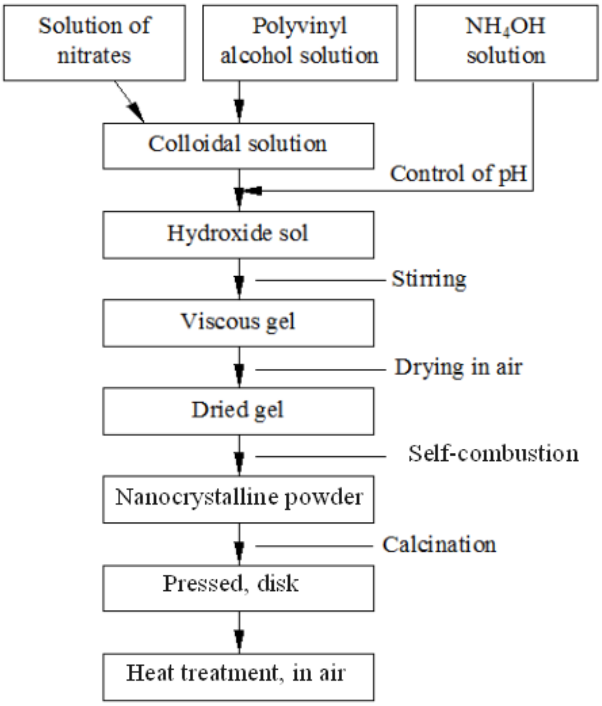


Fig. 1. Processing of materials by self-combustion route.

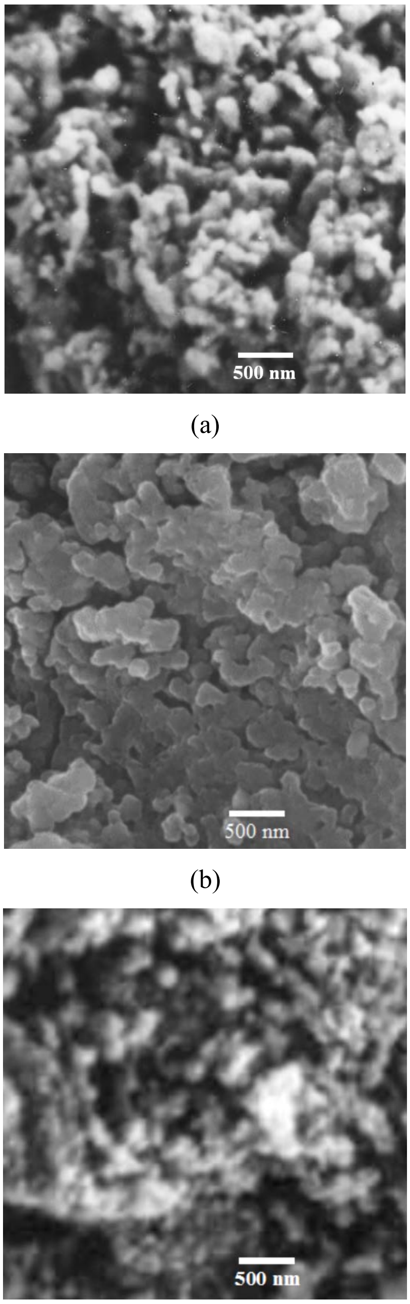
TABLE I. HEAT TREATMENT PARAMETERS AND STRUCTURE CHARACTERISTICS FOR STUDIED SAMPLES.

Sample	**Heat treatment parameters**	**Lattice parameter *a* (nm)**	**Average particle size *D* (nm)**	**Bulk density *d* (g/cm^3)**
NCM	30 min / 1000 °C	0,832	100	3.11
LS	120 min / 850 °C	0.833	150	2.74
MS	240min / 1100 °C	0.835	100	2.52

Generally, the samples display a very fine structure with a pronounced porosity and channels that are favoring the adsorption or desorption of the gas around particle agglomerates. Figure 2 (a, b and c) presents the SEM images of the studied samples, where it is possible to emphasize the extremely fine structure of the granular samples having mean sizes of about 100 - 150 nm. The materials are characterized by enhanced intergranular porosity, 46% for NCM sample, 36% for LS sample and 51% for MS sample. The bulk density was estimated to be in the range of 2.52 - 3.11 g/cm^3. The gas sensitivity of samples strongly depends on their microstructural characteristics.

B. *Electric and acetone sensing properties*

The resistivity of the samples at room temperature are of the order 10^9 Ω·cm. The samples show p-type (NCM) and n-type (LS and MS) semiconductor characteristics within the studied temperature range (100 - 420 °C). The thermal activation energy is between 0.5 eV (LS) and 0.6 eV (NCM and MS).


(a)

(b)

(c)

Fig. 2. SEM micrographs for the studied samples, NCM (a), MS (b) and LS (c).

Regarding gas sensing properties, the electric response (in terms of electric resistance) upon exposure to acetone vapors in air was investigated. In Fig. 3 the sensitivity curves for the studied samples are presented, according to the working temperatures. The gas sensitivity is known to be strongly conditioned by the operating temperature, material composition, average particle size, as well as porosity [18, 26].

In the studied operating temperature range, the sensitivities increase with the increase of the temperature reaching maximum values (at temperatures called optimal operating temperatures) then the sensitivities decrease slightly. For NCM sample the sensitivity is 4.5 at the optimum working temperature of 215 °C, while for MS sample the sensitivity is 0.82 at the optimal working temperature of 380 °C, when these samples were exposed to saturated acetone vapors. For sample LS, a sensitivity of 0.83 is obtained at the optimal working temperature of 355 °C, when exposed to a concentration of 200 ppm acetone vapor.

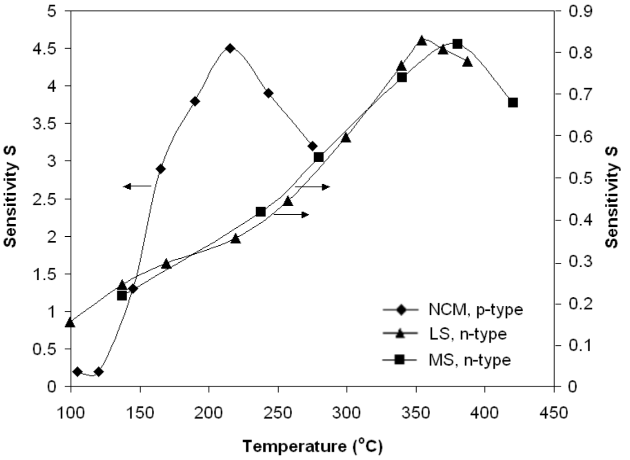


Fig. 3. Temperature dependent sensitivity of studied samples, to acetone vapors.

Due to the oxidizing reaction, in spinel-type oxide semiconductors, oxygen vacancies (as point defects) occur, resulting in the change of electric conductivity of samples (the electron concentration increases in samples with *n*-type semiconductor behavior, while the hole concentration is increasing in the case of *p*-type samples).

Several experiments have been repeated on samples exposed in acetone vapors and the obtained results were found to be reproducible. It can be supposed that the enhanced sensitivity of these compounds to acetone involves a possible reaction of acetone with the spinel-type material surface, resulting in an increased sensitivity. Considering, for example, the NMC sample, which is a *p*-type semiconductor material, when this sample is exposed to acetone atmosphere, a chemical reaction takes place between C_3H_6O and the adsorbed oxygen:

$$C_3H_6O + 8\cdot O^{n-}(ads) \rightarrow 3\cdot CO_{2ads} + 3\cdot H_2O_{ads} + 8\cdot ne \qquad (2)$$

So released electrons would annihilate the holes present in respective material. Thus, the sample resistivity will increase. Each acetone molecule will be responsible for the supply of 8n electrons. Therefore, further clarification of the surface reaction mechanism of acetone will require supplementary investigations.

Some important factors for every gas sensor are represented by the response and recovery times, when the sensor is exposed to the gaseous ambient and then removed from it [22]. The response time required for attaining a response value of 90% of its maximum value is ~3 min. The time taken by the sensor element to come back, once the test gas is removed, was found to be longer, of 4 to 6 min.

IV. CONCLUSION

Structural, morphological and sensory characteristics of three porous oxide semiconductors, $Ni_{0.99}Co_{0.01}Mn_{0.02}Fe_{1.98}O_{4-\delta}$ (NCM), $Li_{0.5}Sm_{0.1}Fe_{2.4}O_4$ (LS) and $Mg_{0.9}Sn_{0.1}Fe_2O_4$ (MS) have been presented. The compounds were synthesized by self-combustion technique. After the thermal treatments in air the studied samples show a spinel structure. The samples exhibit a very fine structure (about 100 nm) with an enhanced porosity (about 46%) and channels that favor the adsorption or desorption of the gas around particle agglomerates. Samples show a semiconductor behavior with thermal activation energy between 0.5 and 0.6 eV. The gas sensitivity is strongly influenced by the operating temperature, material composition, particle size and porosity.

For NCM sample the sensitivity is 4.5 at the optimum working temperature of 215 °C, and for MS sample the sensitivity is 0.82 at the optimal temperature of 380 °C, upon sample exposition to saturated acetone vapors. For sample LS, a sensitivity of 0.83 is obtained at the optimal working temperature of 355 °C, when exposed to a 200 ppm acetone vapor atmosphere. Investigated compounds hold promise for high-performance applications in acetone sensors.

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