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HYDROGEN MICROSENSOR BASED ON NIO THIN FILMS

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Abstract – A multitude of industries use H_2 either as part of their process or as a fuel. All these applications motivate nowadays the development of hydrogen sensor devices which enable its safe and controlled use. Since H_2 is explosive above the lower explosion limit at 40,000 ppm, devices which permit the detection of its presence and measure its concentration become indispensable. In this work, we present a microsensor based on NiO thin films produced with dc reactive magnetron sputtering on GaAs, with an incorporated Pt heater, all on a DO-8 package ready for use. The microsensor was tested to H_2 concentrations 5,000 and 10,000 ppm at different working temperatures. The change of the electrical resistance of NiO thin films was the signal for hydrogen sensing. The response of the sensor was not proportional to concentration of the gas neither to the working temperature.

Keywords: NiO, H_2, gas sensors

1. Introduction

Hydrogen as an industrial gas is being used by a multitude of industries. Some of the major industries today are chemical industries (refining crude oil, plastics, reducing environment in float glass industry, etc.), food industry (hydrogenation

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of oils and fats), semiconductor industry (as processing gas in thin film de-position and in annealing atmosphere), transportation (as fuel in fuel cells, rockets for space vehicles) and use H_2 either as part of their process or as a fuel.[1]

All these applications necessitate the development of hydrogen sensor devices which enable its safe and controlled use. Since hydrogen is explosive above the lower explosion limit (LEL – 40,000 ppm) devices which permit the detection of its presence and its concentration become indispensable.[2]

Nickel oxide (NiO) is frequently considered as a model for p-type semiconductors. It is a wide band-gap ($E_g \approx 4$ eV) transition metal oxide, with a cubic rock-salt structure and antiferromagnetic properties below its Néel temperature, 523 K.[3] Due to their excellent chemical stability NiO films have a wide range of applications as catalysts,[4] electrochromic display devices[5] and fuel cells.[6] Moreover, recent works have shown that thin NiO films are attractive sensing material in gas and humidity detection devices.[7,8]

NiO thin films have been deposited by different techniques, including chemical self-assembly,[9] sol-gel,[10] RF,[11] DC sputtering[12] and recently pulsed laser deposition (PLD).[6,13,14] The preparation method is fundamental in determining the microstructure and consequently the functional properties of the synthesized materials. In this work we demonstrate the response of NiO thin films to hydrogen.

2. Experimental

The different layers of the microsensor were deposited by dc reactive magnetron sputtering on a GaAs substrate (Figure 1). By using a suitable mask and photolithographic process, platinum integrated heater having a shape of meander was realized. A layer of polyimide was deposited on Pt heater for electrical isolation. At the top NiO thin films were deposited. The microsensor was placed on a DO-8 package ready for use. The sample was mounted inside a gas test chamber which was evacuated at 10^{-2} mbar.

The chamber was filled with dry air and then heated at different temperatures. The microsensor was tested at 5,000 ppm (working temperatures 210ºC, 240ºC and 280ºC) and 10,000 ppm (working temperatures 185ºC and 205ºC) of H_2. The concentration of hydrogen was calculated using the partial pressures of the sensing gas and air in the chamber. The change of the electrical resistance of NiO thin films was the signal for hydrogen sensing.

3. Results and Discussion

The response of the microsensor at 5,000 ppm (working temperature 240ºC) and at 10,000 ppm (205ºC) of H_2 is seen at Figure 2. The response of the sensor

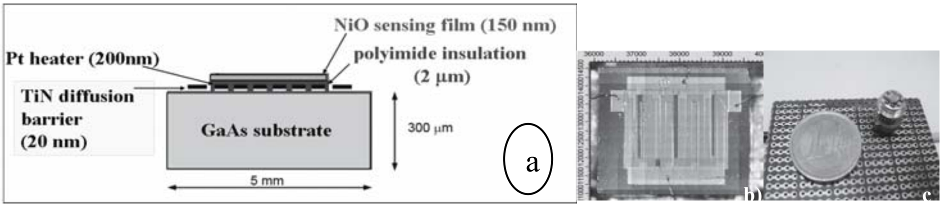

Figure 1. (a) The structure of the microsensor, (b) image of the surface of the microsensor, (c) photograph of the microsensor.

was not proportional to the concentration of the gas neither to the working temperature.

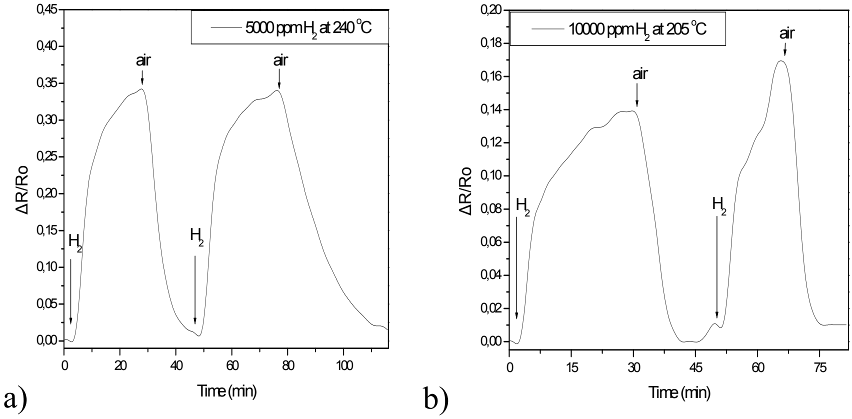

Figure 2. (a) The response of the sensor at 5,000 ppm, (b) the response of microsensor at 10,000 ppm.

The increase of the electrical resistance was expected, considering that NiO is a p-type semiconductor and hydrogen is a reducing gas. As it is known, the NiO p-type conductivity is due to the non-stoichiometry of the prepared samples, in which vacancies occur in cation sites, i.e. the NiO films showed a metal deficiency.[15]

Atmospheric oxygen is expected to be present on the surface of NiO as $O_{2,ads}^-$ and O_{ads}^- negative charged chemical species. The high coverage with adsorbed oxygen species causes an increase in the concentration of the holes of the NiO film and an increase in its conductivity. The presence of H_2 causes a decrease of the electrical conductivity, because H_2 reacts with adsorbed oxygen and forms water vapor, injecting electrons in the NiO p-type semiconducting film[2]:

$$2H_2,gas + O_2,ads^- \leftrightarrow 2H_2Ovap + e^-$$

$$H_2,gas + Oads^- \leftrightarrow H_2Ovap + e^-$$

4. Conclusions

A NiO microsensor has been developed by DC Magnetron Sputtering. The sensor's response to H_2 down to 5,000 ppm has been recorded. The resistance increased as expected for a p-type semiconductor in a reducing gas atmosphere.

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