HYDROGEN SENSING AND PHOTOELECTRIC PROPERTIES OF GRAPHITE/ZNO NANORODS JUNCTION

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Abstract Hydrogen sensing and photoelectric properties of a graphite/ZnO nanorods (NRs) junction were investigated. The graphite/ZnO NRs junction was prepared by low temperature hydrothermal growth and deposition of colloidal graphite. The proposed hydrogen sensor showed response to 1000ppm hydrogen in nitrogen even at room temperature.

Keywords: ZnO Nanorods, Graphite based junction, hydrogen sensor.

1. INTRODUCTION

The use of hydrogen gas in different technological areas (such as chemical industry, medicine, hydrogen fuelled vehicles, etc.) requires the development of a high sensitivity, short response time, small size and low-cost hydrogen sensor. Zinc oxide (ZnO) has been extensively used as a sensitive material for H_2 detection [1-3]. The sensing process is governed by the oxygen vacancies on the surface of ZnO which influence its electrical properties. Oxygen molecules adsorbed on the surface extract electrons from the conduction band of ZnO to form O^- and O^{2-} anions. This process leads to the formation of a depletion region with reduced carrier concentration near the sample surface. When exposed to hydrogen, the chemisorbed oxygen species react with it, releasing the extracted electrons to the conduction band, and thus decreasing the resistivity [4]. However, hydrogen sensors based on bulk ZnO typically require the use of high temperatures to increase their sensitivity. In contrast, one dimensional ZnO nanostructures present a much larger surface area, which greatly enhances their sensitivity and allows the detection of hydrogen at room temperature.

Recently, hydrogen sensors based on ZnO NRs decorated with Pd or Pt nanoparticles have been reported [5,6]. Pd coated ZnO NRs detected hydrogen in concentrations down to 10 ppm with sensitivities of about 2.6% at 10 ppm and 4.2% at 500 ppm measured at room temperature [5]. The uncoated devices showed a sensitivity of ~0.25% at 500 ppm H_2 in N_2. These ZnO NRs were prepared by molecular beam epitaxy, which involves high working temperature and expensive instrumentation. Wang et al. proposed the use of low cost hydrothermal growth to fabricate a ZnO NRs hydrogen sensor with a sensitivity of about 15% at 200 ppm H_2 in dry air measured at room temperature [7]. I was reported that NRs prepared by this hydrothermal method provide more oxygen vacancies for the effective gas detection. Detection of gas molecules in all these previously mentioned cases was achieved by measuring resistivity changes. In this work we propose the use of a graphite/ZnO NR junction as hydrogen sensor. This structure shows a high sensitivity response of about 80% to 1000 ppm H_2 in N_2 at room temperature.

2. EXPERIMENTAL AND RESULT

2.1 Seed layer preparation

The ZnO seed layer was prepared on a Si substrate with free electron concentrations of 2-3x10^{15} cm^{-3} which was cleaned by a standard RCA cleaning procedure. The solution for the seed layer was prepared by dissolving zinc acetate in ethanol (30mM) at 50 °C and magnetically stirring it for 30 min. This solution was spin-coated on to the Si substrate at 1000 rpm for 30 s and dried at 130 °C for 5 min. This step was repeated several times in order to obtain full coverage and then the sample was annealed at 300 °C for 1h. Fig. 1(a) shows the scanning electron microscopy (SEM) image of the ZnO seed layer, which consisted of a homogeneous deposit of ZnO nanoparticles with very small sizes (about 10 nm in diameter).

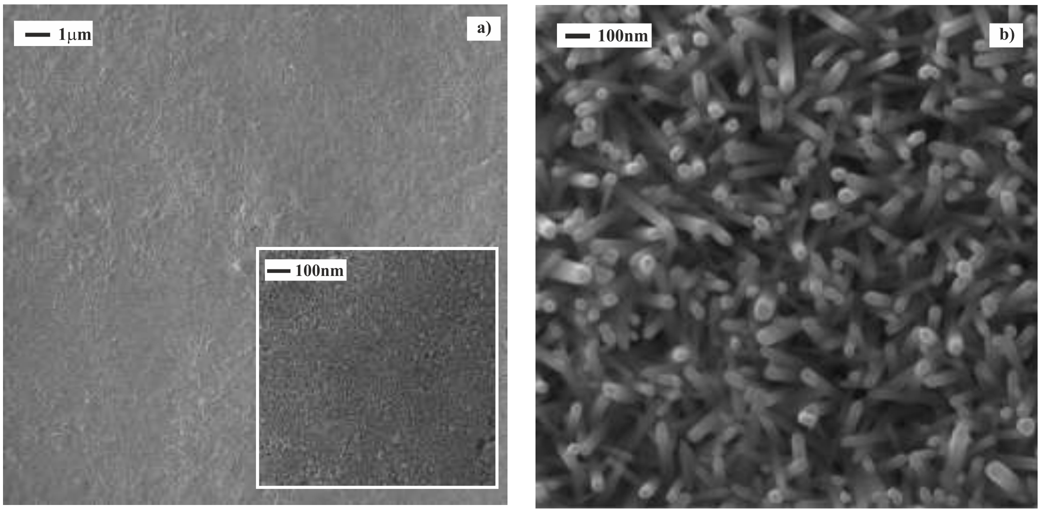

Fig 1. SEM images of the seed layer prepared by spin coating (a) and of the ZnO NR grown by hydrothermal method (b).

2.2 Hydrothermal grown of the ZnO NRs

The subsequent hydrothermal growth of the ZnO NRs was carried out following the procedure reported by Vayssieres [7]: the seed layer was vertically immersed in a laboratory glass bottle containing an aqueous equimolar solution of zinc nitrate hexahydrate ($Zn(NO_3)_2•6H_2O$) and hexamethylenetetramine (HMTA). The bottle was then sealed and introduced in a furnace at 95 °C, where it was left for 3 h. After the procedure, the samples were immediately rinsed with deionized water and dried with argon. The SEM image of the ZnO NRs with average diameter about 30 nm and length about 1 μm is presented in Fig. 1(b).

2.3 Graphite/ZnO NRs junction preparation and their electrical characterization

Recently it was demonstrated that graphite films form thermally stable rectifying contacts on different semiconductor materials [9,10]. Thin layers of graphite contacts can be easily deposited by simple and low-cost drop-casting technique on top of the ZnO NR arrays in order to prepare the graphite/ZnO NRs junctions (for more details see our previous publication [11]). The contact area was checked by optical microscopy to keep the contact size close to 0.7 mm. The ohmic contact, in turn, was prepared with Ga-In paint on a small portion of the seed layer that had been covered by a photoresist before the hydrothermal growth, and which was removed after the procedure. A diagram of the graphite/ZnO NRs junction is shown in Fig. 2a. The current-voltage characteristics of the graphite/ZnO NRs structures show rectifying behavior (Fig. 2b), which confirm the formation of the electrical junction between the graphite film and the ZnO NRs.

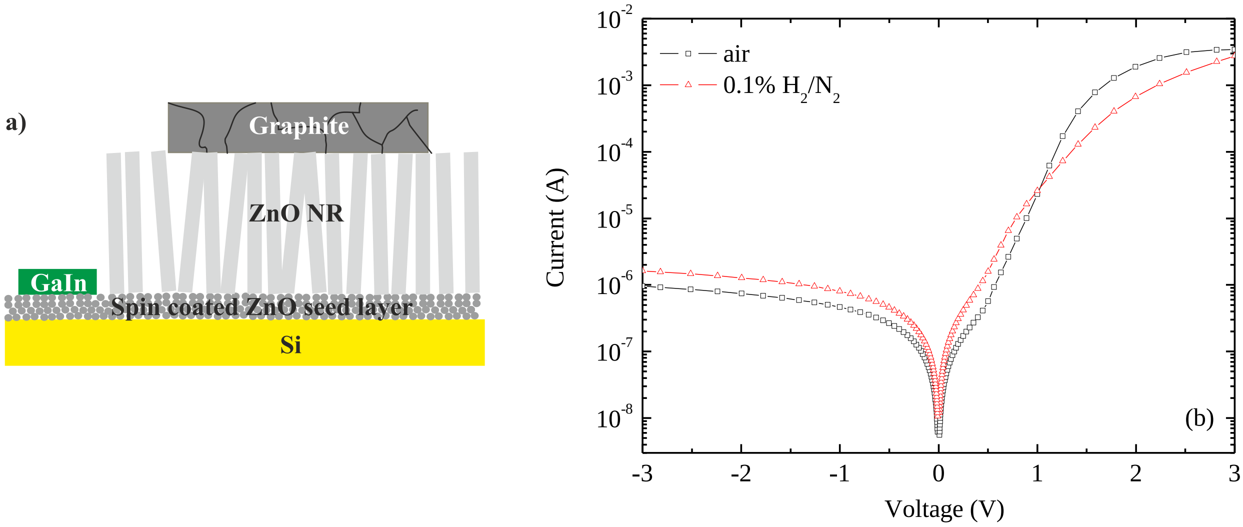

Fig. 2 (a) schematic cross section and (b) current-voltage characteristics of the graphite/ZnO NR junction measured in air and under exposure to 0.1% H_2 in N_2.

2.4 Hydrogen sensor performance

We demonstrate that the graphite/ZnO NRs junctions show response to hydrogen even at room temperature. These structures were tested for their sensitivity to hydrogen in a dark cell with a through-flow gas system. The first preliminary experiments were performed with a mixture of H_2/N_2 containing 1000 ppm of hydrogen (Fig. 3). The current increase is characterized by a sensing response, *S*, of 80%, calculated applying the following equation,

$$S = {(I_H - I_{air})}/{I_{air}} * 100\%$$

where I_H- is saturation current under exposure to hydrogen and I_{air} is the same for air.

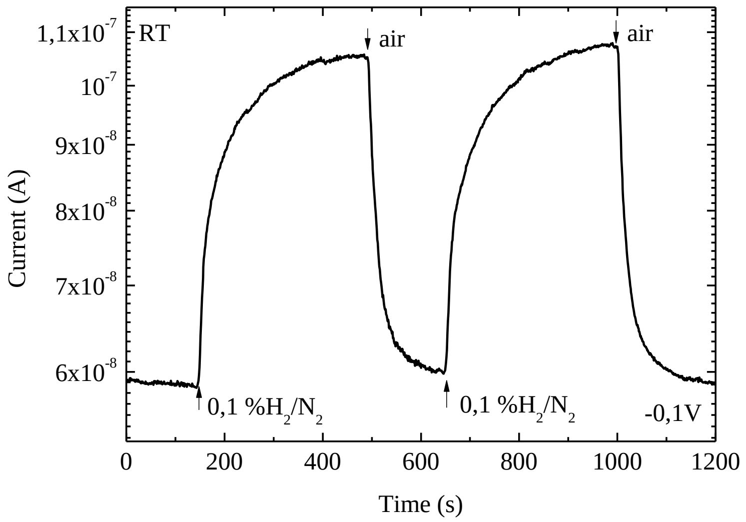

Fig. 3 Current-transient characteristics of the graphite/ZnO NRs junction.

2.5 Photoelectric properties

The photoelectric properties of the graphite/ZnO NRs junction are shown in Fig. 4. These junctions can work under both photoconductive and photovoltaic modes. The ratio between the photocurrent and the dark reverse current I_{ph}/I_{dark} saturated at a value of about 800 under halogen lamp illumination at room temperature. The graphite/ZnO NRs junction generates a short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) of 2 mA·cm^{-2} and 0.28 V, respectively.

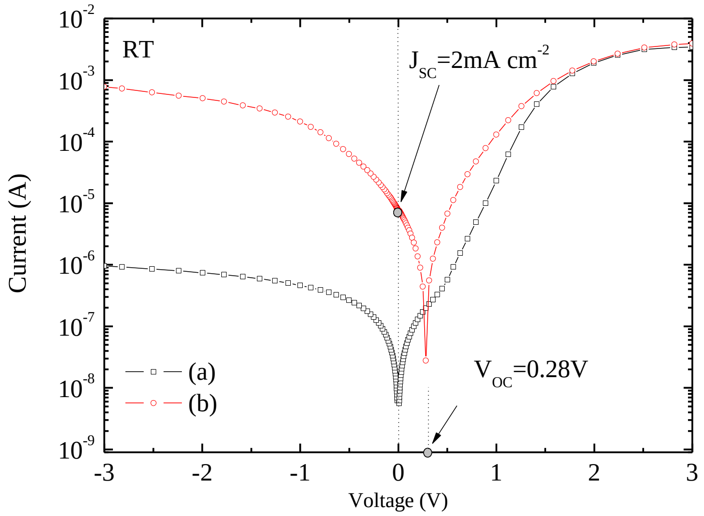

Fig. 4 IV characteristics of the graphite/ZnO NRs junction measured in the dark (a), and under halogen lamp illumination (b).

3 CONCLUSION

We studied the sensing and photoelectric properties of a graphite/ZnO NRs junction, where well oriented ZnO NRs were prepared by hydrothermal growth and the graphite contact was deposited from colloidal suspension. The junction shows a highly sensitive and reversible response to low concentrations of hydrogen at room temperature. The ZnO NRs grown by low temperature hydrothermal method show promising results for low cost and low power levels high sensitivity hydrogen sensors.

ACKNOWLEDGMENT

This work was supported by a EU COST Action TD1105 – project LD14111 of the Ministry of Education CR.

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